

ELECTROLYTIC CONDUCTANCES AND RELATED
PROPERTIES OF SOLUTIONS OF SOME
ACIDS AND SALTS IN ACETONE.

A thesis submitted to the
University of Cape Town for the
Degree of Doctor of Philosophy

by

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SUMMARY

Although a thorough investigation of various methods of preparing pure, anhydrous acetone has been made (cf. Sadie), no investigations of methods for determining the moisture content of this solvent have previously been described. A solvent with a consistently low water content is essential for electrochemical measurements. Accordingly an extensive study of moisture content determination in acetone was made. A modified Karl Fischer titration procedure was found to be most suitable for the very low moisture contents of the acetone used in this work.

All A.C. conductance measurements made using two platinised electrodes are, in some degree, liable to errors due to polarization, end effects and the state of the electrode surfaces. Several workers have also found errors due to the presence of finely divided platinum, such as adsorption of electrolyte on the colloidal platinum, the shaking effect and catalysis of reactions in solution. These errors are reduced by using lightly platinised or bright platinum electrodes, but polished electrodes give rise to increased polarization errors.

In this work conductance measurements were made using a new four-electrode A.C. potentiometer, which employs bright

platinum electrodes enabling conductance measurements to be carried out in acetone without recourse to platinisation, thus avoiding errors due to the presence of platinum black, contact resistances of electrodes and the like. The measurements on this apparatus were shown to be independent of frequency using aqueous potassium chloride solutions, and the accuracy of the results was tested using aqueous sodium chloride solutions.

Perchlorates have been considered by some investigators (e.g. Ross Kane) to be strong electrolytes in acetone solutions and other workers (e.g. Accascina and Schiavo) found the alkali perchlorates to be weak electrolytes. The approximate limiting ionic conductances calculated by these last named workers were at variance with those of other investigators (e.g. Kraus). It therefore appeared that a study of the conductances of solutions in acetone of perchloric acid and some of its salts by the new potentiometric method would be advantageous.

The conductances of three alkali perchlorates and the previously unknown conductances in acetone of ammonium perchlorate, pure anhydrous perchloric acid and lithium chloride were measured by the potentiometric method. Limiting equivalent conductances and dissociation constants were calculated for all the electrolytes and the results discussed. These electrolytes were, in general, found to be relatively weak in acetone,

although perchloric acid is considerably stronger than hydrochloric acid.

The conductance results indicated that the potentiometric method should be generally applicable to electrolyte solutions in all solvents, and can be used to advantage in all cases influenced by the errors previously mentioned.

It is generally recognized that interpretation of conductance data and the development of the theory of electrolyte solutions is seriously hindered by the lack of transport data in non-aqueous solvents. Transference measurements were undertaken using a conductimetric moving boundary method, and a limiting transport number for the anion constituent of potassium thiocyanate was obtained in acetone. This is the first reasonably accurate limiting transport number to have been measured in acetone.

From the equivalent conductance data of this work, and the literature, the first limiting ionic conductances in acetone have been calculated and the results discussed. The limiting conductance of the hydrogen ion, $101 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$, was not found to be anomalous, as for example, in water. Anions were found to have generally higher conductances than cations, which is consistent with the view that cations are, in general, more solvated than anions in dipolar aprotic solvents.

Conductance results of numerous workers have indicated considerable uncertainty about the entities present in acetone solutions of hydrogen chloride.

In order to add to existing knowledge, tracer diffusion coefficients of hydrogen chloride in acetone solutions were measured at 15°, 25° and 35° C over a range of concentrations using hydrogen chloride labelled with chlorine -36. The capillary tube method was used, and concentrations were measured by a scintillation counting procedure. Complete interpretation of the results is impossible in the light of present knowledge, but they appear to be consistent with suggestions, based on conductance measurements in this system, that hydrogen chloride polymers may be present.

TO BRIDGET

PREFACE

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PART I.

INTRODUCTION AND AIMS OF THE PRESENT WORK.

I. 1 Preparation and Purification of Anhydrous Acetone and Determination of its Moisture Content.

Acetone is a very interesting solvent for electrochemical studies. It is an important example of a differentiating, non-hydroxylic solvent with a low viscosity and fairly low dielectric constant. Its enol content of $2.4 \times 10^{-4}\%$ is very low and need not be considered for most work. Practically it has several disadvantages, chief among these being the difficulty experienced in obtaining the solvent free from impurities, especially water. Its vapour pressure of 229 mmHg at 25° is high, and it thus becomes essential to presaturate any gas used as a moisture free atmosphere in order to minimise evaporation losses from solutions. On the other hand, acetone is a satisfactory solvent for a number of inorganic and organic compounds and it is relatively inexpensive.

A considerable number of conductance studies have been made in acetone and the results obtained by different workers do not always agree within the relevant precisions quoted. For example, Sackur,¹ in 1902, found hydrogen chloride to be a strong acid in acetone whereas Mackor and Spaarnay² found it to be weak, with a dissociation constant of about 10^{-7} . In an extensive investigation using KI in acetone solutions, Dippy and Hughes³

concluded that the discrepancies in the results of earlier workers⁴⁻⁹ in acetone were due to variations in the moisture content of their acetone, which had been previously suggested by Reynolds and Kraus.⁸ These last workers⁸ believed that the conductance results of previous investigators were inaccurate due to the high and varying water content of their acetone, which resulted in a high and varying specific conductance for their solvent. The work of numerous investigators^{3,11-17} indicates the importance of using a pure solvent with as low a specific conductance and water content as possible; but, as pointed out by Eck,¹⁸ absolute purification of acetone is impossible and traces of water will always remain.

An investigation of the various methods of drying acetone which include initial desiccation with calcium chloride,⁸ potassium carbonate,⁵ activated alumina,^{3,8} phosphorus pentoxide,¹⁵ and copper sulphate,¹⁹ followed by distillation, was made by Sadie.¹³ The procedure which he found to give acetone with the most consistently low moisture content and specific conductance, involved shaking the solvent over calcium chloride for several days, refluxing and standing over activated alumina for several more days followed by two fractional distillations. The entire dehydration procedure, except for the initial shaking with calcium chloride, was carried out in an atmosphere of dry nitrogen which is, in itself, an improvement

on the procedures of other workers. This purification procedure was used in this work, with modifications designed to increase the fraction of anhydrous product obtained.

Not many workers have measured the moisture contents of their acetone. Mysels²⁰ used the conductances of various halides in acetone to determine the moisture content of his solvent, and he claimed that it was impossible to obtain a water content below 0.05%. Other workers^{8,13,16} have used various modifications of the Karl Fischer titration method. The work described in this thesis relies on the assumption that the acetone used was as free from moisture as possible, and that the water content remained constant from batch to batch. Hence it was decided to undertake an extensive investigation of several procedures used for moisture determinations, and to measure the moisture content of every batch of solvent prepared. The use of molecular sieve as a drying agent for acetone to be used in electrochemical work was also investigated.

I. 2 Conductance and Transference Studies in Acetone.

As mentioned in the previous section, numerous conductance studies on a wide variety of solutes have been made in acetone, the results of separate workers not always agreeing. One possible reason for these differences may be varying moisture content of the solvent, another may be the presence of other impurities and yet a third is probably the instability of acetone

in the presence of certain electrolytes. An example of a solute where different conductance results are probably due to all these reasons is perchloric acid. Its solutions are known to be unstable over a period of time and have been seen to change colour on standing,^{9,13} probably due to self condensation of the acetone. Ross Kane⁹ prepared solutions of this acid in acetone by chemical reaction as did Coetzee and McGuire,¹² who claimed that the presence of acetic acid in such solutions would not affect the conductance results. Sadie¹³ prepared solutions of pure acid in acetone, but his results were inconclusive in that a negative dissociation constant was obtained from the Fuoss plot. Sadie¹³ suggested that enhanced enolisation of acetone in acid solutions, catalysed by the platinum black on the electrodes in the conductivity cell, may affect the results.

Kraus and co-workers^{21,22} found adsorption errors occurred when using large, platinised electrodes to measure conductances in organic solvents at low concentrations. This indicates a need to use unplatinised electrodes where possible. In addition conventional¹⁰ two electrode A.C. conductance measurements are often in some degree liable to errors due to polarisation¹⁷ and end effects. In 1957 a prototype instrument for measuring electrolyte conductance by a method using four bright platinum electrodes was developed in

co-operation with this laboratory.²³ The prototype instrument could not be used with acetone solutions because of its limited resistance range. However, the instrument has since been completely redesigned and specially modified for conductance measurements of high resistances as required in this work. The conductance studies described in this thesis are the first with the new four electrode A.C. potentiometer and were not affected by end effects, polarisation errors or errors due to the presence of platinum black.

In view of the uncertainty as to the conductance of pure, anhydrous perchloric acid in pure, dry acetone the conductance of this acid was measured by the new potentiometric method. The conductances of three alkali perchlorates and ammonium perchlorate were also measured, the first three in view of the results of Accascina and Schiavo¹¹ for these salts which produced approximate ionic conductances at variance with those of other workers,^{5,8} and the last named salt because its conductance was unknown. In addition Ross Kane⁹ had found all his perchlorates to be strong electrolytes in acetone, whereas Accascina and Schiavo¹¹ had found the alkali perchlorates to be relatively weak. The conductance of lithium chloride was measured as it seemed possible that this salt may have proved useful in transference measurements and its conductance was also unknown.

Although a vast amount of conductance work has been performed in many solvents, it is generally recognised that the interpretation of these results is being severely handicapped by a lack of transport numbers,²⁴ and hence ionic conductances, in these solvents. Acetone is no exception and transport numbers have not previously been determined in this solvent. Earlier attempts to measure accurate transport numbers in acetone were made by Erdey-Gruz²⁵ and Sadie¹³ using the e.m.f. method for hydrogen chloride solutions. However, they were unsuccessful in that a limiting value of t_{H^+} at infinite dilution could not be found, apparently because of excessively high cell resistances.

In view of the urgent need for transport measurements in acetone it was decided to attempt such measurements. The moving boundary method was selected as the most suitable for obtaining precise results and the boundary movement was followed by a conductimetric method.²⁶ These transference measurements in acetone bring the total number of non-aqueous solvents for which precise transport data are available to only seven. The conductance results could then be further interpreted in the light of the calculated values of the ionic conductances.

I. 3 Diffusion of Hydrogen Chloride in Acetone.

The conductance of hydrogen chloride in acetone has been measured by Sackur,¹ Mackor and Spaarnay,² Ross Kane,⁹ Sadie¹³ and Hotz¹⁶ at 25° and by Dorofeeva and Kudra²⁷ from -21.2° to 0° C. All these workers, except for Sackur, found that hydrogen chloride solutions in acetone were unstable over a period of time and concluded that the acid was an extremely weak electrolyte in such solutions. Mackor²⁸ suggested that HCl dimerised in acetone and Hotz suggested that polymers of up to twelve HCl molecules could exist. Janz and Danyluk²⁹ have mentioned the possible existence of various $(\text{HCl})_x-(\text{acetone})_y$ complexes and Braude³⁰ has shown the existence of $(\text{CH}_3)_2\text{COH}^+$ in such solutions. Sadie¹³ measured diffusion coefficients of hydrogen chloride in acetone at 25° but his results were generally irreproducible.

In an attempt to resolve some of the uncertainties about the entities present in the hydrogen chloride - acetone system, the tracer diffusion coefficients of H^{36}Cl were measured at 15°, 25° and 35° as a function of concentration. The results were obtained using scintillation counting procedures rather than Geiger-Muller counting,¹³ which improved the precision of the results very considerably.

PART II.

PURIFICATION OF THE SOLVENT AND

DETERMINATION OF ITS MOISTURE CONTENT.

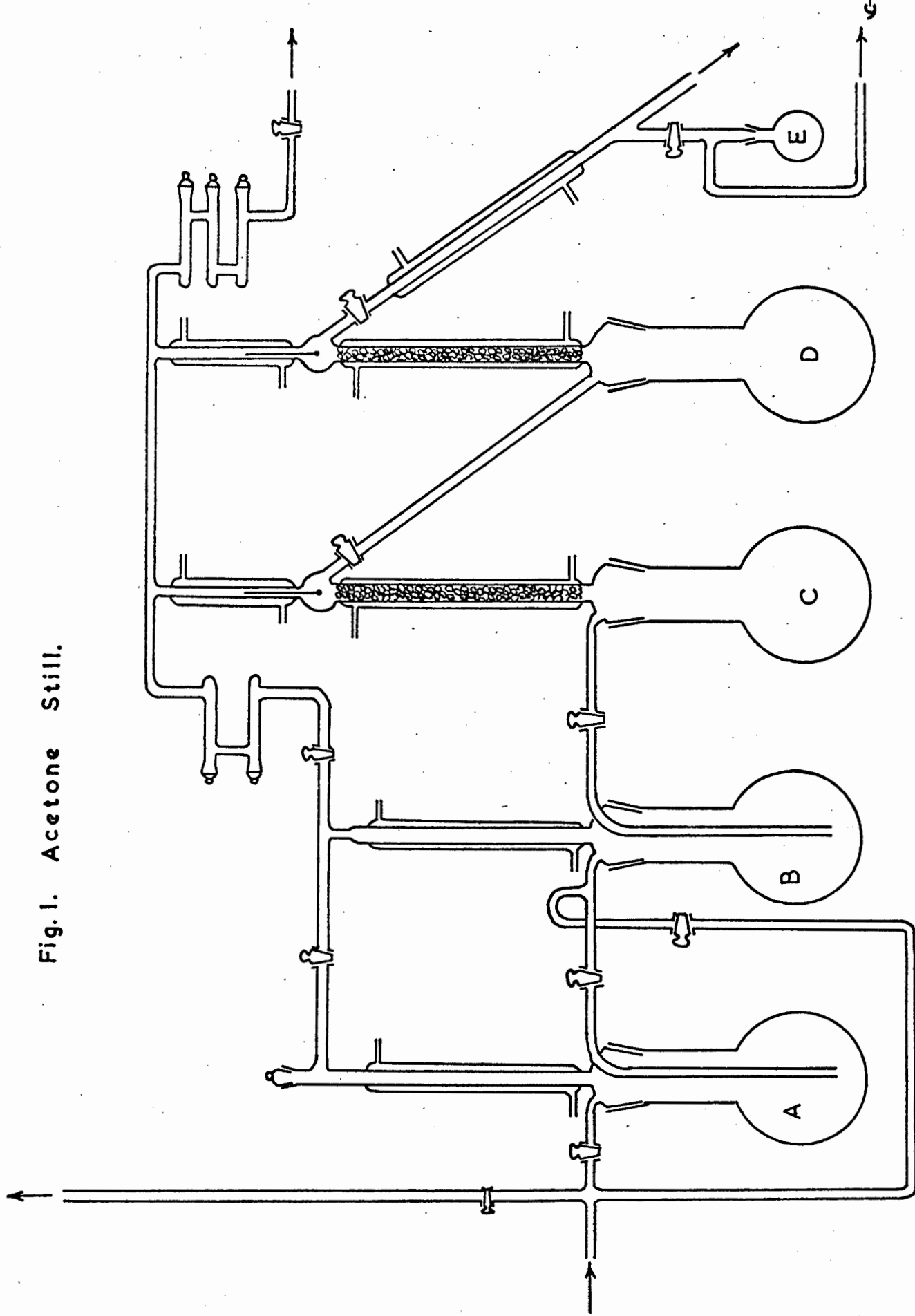
II. 1 Preparation of Anhydrous Acetone.

Kraus⁸ has stated that conductance measurements must be performed in solvents of very high purity, particularly with regard to their specific conductance, otherwise such measurements are not worth making at all. Mysels²⁰ found the conductance of many electrolyte solutions in acetone to be strongly dependent on the moisture content of the solvent, as did Ross Kane.⁹

In this work a variation of the method of Sadie,¹³ which was a modification of Dippy and Hughes,³ procedure, was used to prepare pure anhydrous acetone. The alterations to the method and to a well-seasoned still,¹³ which had been used for about seven years exclusively for the preparation of anhydrous acetone, were designed to increase the yield of anhydrous product. Great care was taken to ensure that the solvent used would be consistently of the highest quality obtainable. The preparation procedure will be briefly described below.

The starting material throughout this work was Riedel de Haen Analar acetone. Flasks A, B, C and D (fig.4) having been dried at 120° before use, one litre of acetone, which had been shaken over calcium chloride for three days, was filtered on to Spence Type A activated alumina pellets in the first reflux flask A. The acetone was refluxed under dry nitrogen in flask A for three hours, and then allowed to

Fig.1. Acetone Still.



stand isolated from the rest of the still for two days. Refluxing and standing were carried out in dimmed light, and with several thicknesses of black cloth wrapped round exposed portions of the flasks.

The liquid was then blown, with dry nitrogen, into flask B, containing fresh alumina, and the refluxing and standing procedure repeated. The liquid, which had attained a yellow colour by this stage, was blown into the first fractionation flask C and slowly fractionally distilled through a 1.1 metre glass column packed loosely with $\frac{1}{8}$ " Dixon gauze rings. Only about four fifths (800 ml) of the liquid was distilled over into flask D, where a similar fractional distillation on the now colourless acetone was performed. The first 20 ml of distillate from this final fractionation was collected in flask E, the remainder, except for about 25 ml, being collected in a dry box in a special receiver (fig. 2a) designed by Hotz¹⁶. Each fractional distillation took about six hours, the undistilled fractions being discarded. Distillations were performed in dim light.

The steel and glass dry box and the entire distillation apparatus were kept under a positive pressure of dry nitrogen throughout the above procedures and during all manipulations in the dry box. A mercury safety valve prevented the nitrogen pressure in the apparatus exceeding two centimetres of mercury above atmospheric pressure at any stage. The nitrogen was passed through a drying train consisting of two tubes of indicating silica gel and four tubes of phosphorus pentoxide which were frequently changed. The nitrogen was saturated

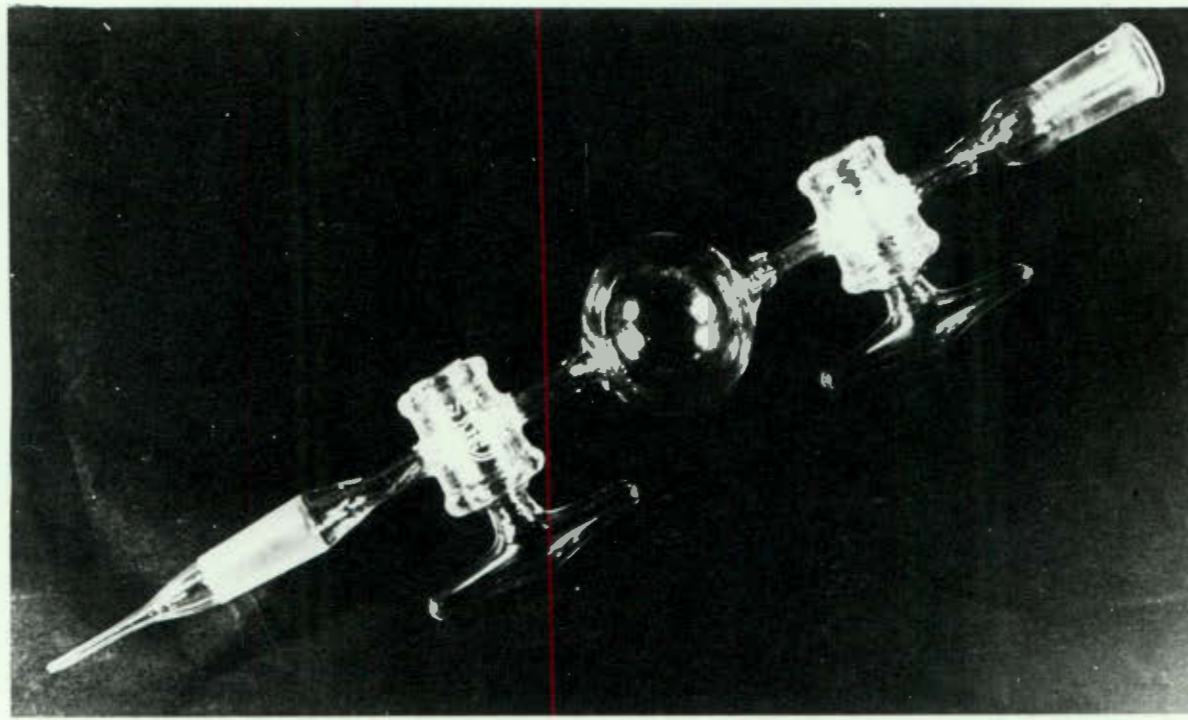
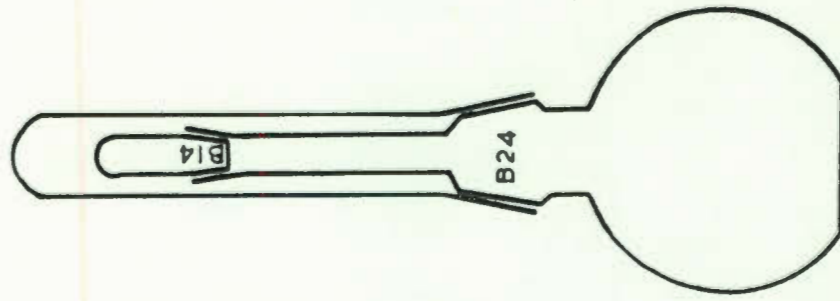


Fig-2a. Acetone receiver. Fig.2b. Weight Pipette.

with acetone before entering the dry box, thus reducing errors due to solvent evaporation from solutions. The dry box was fitted with Neoprene gloves sealed on the outside (to protect the adhesive from attack by acetone) to the front glass wall of the box with adhesive cement. The box, which was flushed with dry nitrogen for half an hour before use, was covered with black paper to make it almost light tight on all sides except for the observation window. Acetone was thus stored in semi-darkness. The receivers (fig. 2a) mentioned above, of one and two litre capacity, enabled anhydrous acetone to be stored for at least two weeks in the dry box without any detectable increase in moisture content or specific conductance over this period. Dry acetone was always used within eight days after the final fractionation and usually within three days.

Dimmed light was used to reduce the possibility of photolytic reactions of the acetone. Sadie found no deleterious effect on the quality of the solvent due to using dim light instead of darkness as suggested by Dippy and Hughes.³ The yellow colouration mentioned previously was due to the presence of self-condensation products of acetone, which were removed by distillation, the formation of which is catalysed by the basic alumina desiccant. Sadie found alumina gave acetone of consistently low specific conductance which was not the case with CaSO_4 or BaO . Each batch, about 200g, of alumina was used a maximum of four times and then discarded because the acetone became a deep yellow on refluxing with the much used desiccant.

The modified procedure and apparatus enabled 750 ml of anhydrous

acetone to be prepared in 9 days as opposed to 600 ml in 14 days using the original method and apparatus.¹³ The quality of the final product was similar to that obtained by the unmodified procedure which gave acetone with ca. 0.003% water, and specific conductance of ca. $1.3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm.}^{-1}$

Several conventional drying agents were tested by Sadie and, as mentioned above, activated alumina pellets were found to give the most consistent results, although considerable wastage occurs due to condensation reactions. During the latter part of this work the suitability of Linde Molecular Sieve 4Å $\frac{1}{16}$ " pellets was tested. The use of this molecular sieve as a drying agent for various solvents has been described by Meeker and co-workers.³¹ A recent publication³² shows molecular sieve drying to be, in fact, one of the most efficient and rapid drying methods. About 200g of the sieve was placed in the 1 litre flasks A and B (fig 1) and the acetone which had been dried over calcium chloride was further dried for periods of up to 48 hours in flask A and then in B. This was followed by two fractional distillations as before. Karl Fischer moisture determinations (II.2.1) were carried out on the product. The results, together with those of specific conductance measurements, as shown are in Table 1. The detection limit was about 0.001% water, and the precision with which a measurement could be made was $\pm 0.001\%$.

Molecular sieve 4Å is thus seen to reduce the moisture content to a level comparable to, if not better than, that obtained by the use of activated alumina within 48 hours. It should be noted that the last four moisture contents shown in the table are in fact equivalent.

TABLE 1.MOISTURE IN ACETONE DRIED WITH MOLECULAR SIEVE

Total Drying Time (hrs)	Moisture (wt%)	Sp. cond. $\times 10^8$
6	0.020	-
12	0.016	-
24 } Flask A	0.005	-
48 }	0.002	7.5
72 } Fresh Sieve	0.003	-
96 } in flask B	0.002	9.2
plus double distillation	0.001	0.8

Particularly noteworthy is the reduction in drying time from about four days over alumina to two days over molecular sieve, and it was also observed that loss of acetone to condensation products was considerably reduced. It can be seen from the table that the double fractional distillation markedly improves the specific conductance, which is slightly better, perhaps, than that of the alumina method which varied from about 0.9 to $1.3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. No direct correlation could be found between specific conductance and water content which suggests that other impurities may be important. It is interesting to note that Lannung²⁰ obtained a specific conductance of about 10^{-10} with a moisture content of 0.2%, although nothing even approaching this has been achieved before or since. Dippy and Hughes³ found a specific conductance of $\text{ca. } 2 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ and Reynolds and Kraus⁸ $1-2 \times 10^{-9}$.

Although the use of molecular sieve in place of activated alumina is somewhat more rapid and efficient, all of this work was nevertheless carried out with acetone prepared by the

modified alumina method, which has been shown¹³ to give acetone of a consistent quality, in order to keep variation in solvent quality to a minimum throughout the entire work. The molecular sieve drying procedure outlined above is recommended for future work.

II.2. Determination of the Moisture Content of the Solvent.

2.1 Introduction

Most of the work described in this thesis relies on the assumptions that the acetone used was really free from moisture and that the moisture content remained constant from batch to batch. As no evidence for these assumptions is available, an extensive study was undertaken to this end, and also to determine which moisture analysis procedures were most suitable.

Previous workers³ have used the Karl Fischer titration method suitably modified for moisture determination in ketones,¹²⁶ and a similar procedure was used in this work. In view of possible side reactions¹²⁶ obtained with K.F. reagent in acetone, and as the determination is rather tedious (and unpleasant, with pyridine) it was thought that investigation of other procedures may prove profitable.

2.2 Karl Fischer Titration Methods.

Dry acetone was found to be extremely hygroscopic, and hence a glass and polythene apparatus¹⁶ with no rubber parts was used to achieve consistent titration results. A tared, clean, dry weight pipette (fig. 2b) was reweighed after filling with acetone in the dry box, and fitted via a ground glass joint with P.T.F.E. sleeve

to the titration vessel of the Karl Fischer apparatus. The two stopcocks of the weight pipette and those of the K.F. apparatus were greased with Fischer "Non-aq" stopcock grease near the bores and with Edwards high vacuum soft grease on the remaining outer portions. Non-aq grease is insoluble in acetone, but affected by water, and Edwards grease is soluble in acetone. The apparatus was flushed with dry nitrogen before the acetone was run into the titration vessel and titrated. The vessel was fitted with a magnetic stirrer and platinum electrodes were used for determination of the end point potentiometrically by iodide depolarisation. The end point detector was a new 'magic-eye' titrimeter kindly given by the Research Department of African Explosives and Chemical Industries Ltd.

The reagent has been described by Mitchell and Smith¹²⁶ and modified for acetone by Ehmke,¹²⁷ and consists of a mixture, standardised for water equivalent, of 270 ml dry pyridine, 683 ml dry benzene, 45 ml (64g) SO₂ and 84.7g iodine. Substitution of the methanol in the conventional reagent¹²⁶ by benzene overcomes the tendency of carbonyl compounds to form acetals or ketals by reaction with the methanol with release of water. Other methods of overcoming this problem have been suggested by Fischer and Schiene³⁷ and Smith⁴⁰, such as converting the carbonyl group to the cyanhydrin. However water contents below 0.1% were not determined by the cyanhydrin method, and considerably lower moistures, ca. 0.002%, could be determined with the reagent used in this work, with an absolute error of about 0.001%. The pyridine was dried over sodium hydroxide and distilled. The benzene

was initially dried over calcium chloride, distilled, and then stored over sodium wire. The reagent was standardised with water directly before use, and as every batch of acetone used for this research was tested, this proved rather tedious.

The moisture content of the acetone used in this research was never more than 0.005%. As a check on the accuracy of the method, acetone-water solutions were prepared using the dry acetone as a blank and adding weighed portions of water. The results are shown in Table 2.

TABLE 2.

MOISTURE DETERMINATION BY KARL FISCHER TITRATION.

Blank (Wt% water)	Water Added (Wt%)	Additional Water Found (Wt%)
0.003	0.002	0.002
	0.005	0.006
	0.010	0.011
	0.020	0.021
	0.100	0.100

From Table 2 it can be seen that with a precision of $\pm 0.001\%$ the method gives satisfactory results.

The moisture content of the acetone obtained from the well-seasoned still described earlier (II. 1) was not only low, but remained consistently so over the four years during which it was tested.

Fischer and Schiene also suggested replacing the methanol with pyridine giving an 'all pyridine' reagent. This reagent was prepared and used as described above. It was found that the results obtained were exactly similar to those found here (Table 2). This reagent thus appears to be equally satisfactory.

2.3 Infra-red Spectrophotometric Methods.

a.) Using the infra-red spectrum near $5,290\text{ cm}^{-1}$.

Many workers have found that water can be rapidly and easily determined in liquids such as glycerol, ethylene, methanol and nitric acid.^{35,129,130} The procedure, which involves using the near infra-red overtone band of water near $5,290\text{ cm}^{-1}$, has been applied to alcohols, amines, ethers, ketones and esters.³¹ The essential features involved are the preparation of a 'dry' reference sample and measurement of the absorbance of the test solution near 1.9μ relative to that of the reference sample.

In this work the reference sample was dried for 96 hours with Linde 4A molecular sieve as described in part II.1. The spectra were run on a Unicam S.P. 100 spectrometer using ca. 0.5 cm variable path lengths, with the molecular sieve dried sample in the reference beam and the alumina dried test solution in the sample beam.

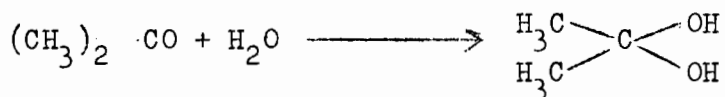
Meeker³¹ found the limit of accuracy for this method to be $\pm 0.02\%$ absolute, in the range 0.02 to 1.00% water. Results obtained in this work showed the reference and sample solutions to have similar water contents in that no significant peaks could be detected. This was not exactly unexpected as the previous discussion has shown. The crux of the matter appears to be that the sample solution must have a moisture content about 0.02% above that of the reference sample for accurate measurements to be obtained. Since in this case the two samples were probably of similar water content and both far below 0.02% water, this method, even with this Unicam S.P. 100 instrument,

is thus inferior to the Karl Fischer at these low moisture contents.

Recently Pearson³³ has suggested the accuracy of this method can be increased to $\pm 0.004\%$, but only above the 0.075% water level.

b.) Using the infra-red spectrum near $3,600\text{ cm}^{-1}$.

Errera³⁴ studied the spectrum of acetone in the $3,000 - 3,700\text{ cm}^{-1}$ region. He concluded that acetone is an 'active solvent', because it gives rise to strong molecular forces between the solvent and water molecules. It seems possible that intermolecular hydrogen bonding will occur between water and acetone, as well as bonding such as



which may explain the great difficulty experienced in drying this solvent. At low (ca. 1%) water contents, Errera found a double band at $3,500\text{ cm}^{-1}$ which he ascribed to a monomer of water. As the water content rose this double band converged into a single one. Gaspart and Gillo³⁶ in 1939 also found a double band, but do not indicate the water content of their reference sample of 'pure, dry' acetone with which the wet samples were compared. Lucchesi,³⁸ in 1956, using 'dry' acetone with 0.5% added water obtained spectra similar to those of Gaspart and Gillo near $3,600\text{ cm}^{-1}$. He did not determine water contents below 0.2% , and his average deviation using this infra-red method was $\pm 0.08\%$.

In this work spectra were run from $3,400$ to $3,650\text{ cm}^{-1}$ on the anhydrous acetone and on a sample with a water content of 0.12% by K.F. titration. The cells had IR - TRAN windows, and fixed path lengths of 0.100 mm , 0.012 and 0.007 mm were used, as obtained with Teflon

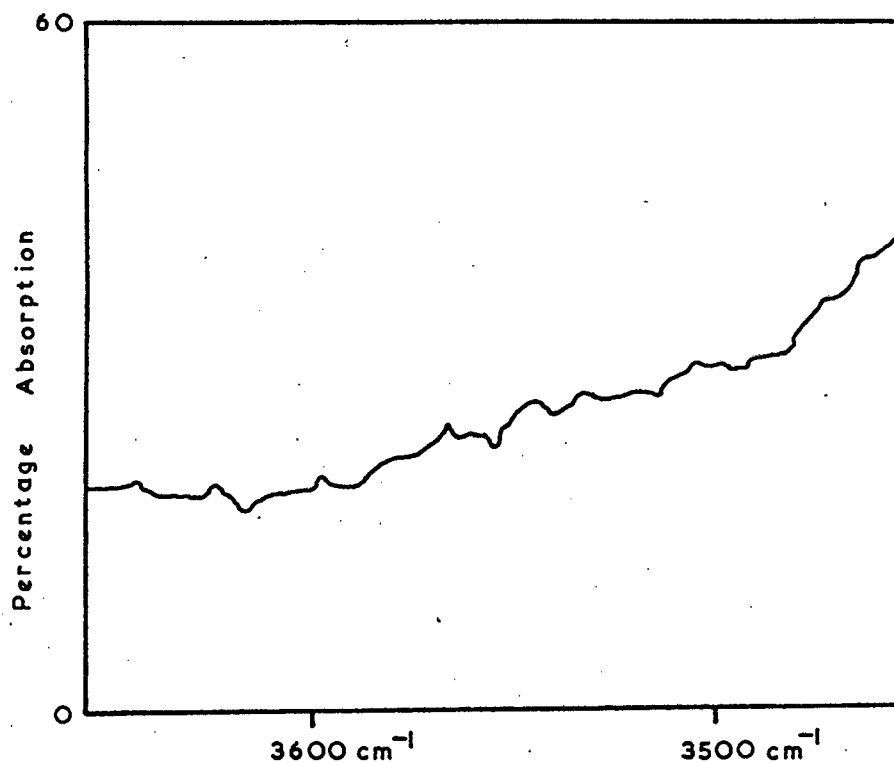


Fig. 3a. Infra-red spectrum of acetone with $<0.005\%$ water.

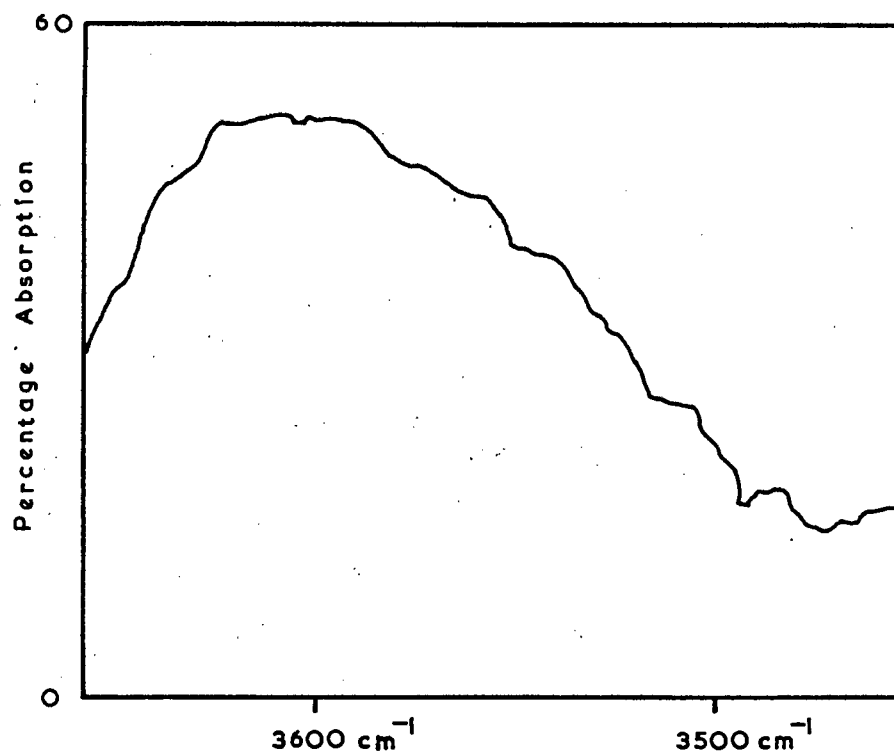


Fig. 3b. Infra-red spectrum of acetone with 0.120% water.

spacers. The 0.100 mm spacers gave the best results since the absorbance with the lower path lengths was too small around $3,600\text{ cm}^{-1}$. It should be noted that good spectra of acetone are very difficult to obtain as tests with variable path length cells initially showed. However, as these cells could not be closed to give very small path lengths, unfortunately, fixed path length cells were obtained. Path lengths of 0.100 mm produced peaks far greater than 100% absorbance on many parts of the spectrum, but were the best obtainable in this case near $3,600\text{ cm}^{-1}$. The dry sample (alumina dried) was placed in the sample beam and an empty, but otherwise similar, cell placed in the reference beam.

The spectra obtained are shown in fig. 3a for the drier sample and 3b for the wetter one. It can be seen that no suitable sharp peak whose absorbance could be accurately measured was found in the $3,500 - 3,650\text{ cm}^{-1}$ region. Since such a relatively small intensity difference for about 0.12% water is obtained, accurate measurement of less than 0.005% water does not appear feasible. Hence it was concluded that the pure acetone used in this work had a moisture content too low to be measured accurately by this method. No moisture determinations using the ca. $3,600\text{ cm}^{-1}$ region have been found subsequent to that of Lucchesi.³⁸

2.4 Using Acetyl Chloride.³⁹

A method⁴¹ based on the reaction of water with acetyl pyridinium chloride³⁹ has been used to determine water in acetone. The method involved preparing a standard 0.5 N NaOH solution. Then an acetyl chloride-toluene reagent was prepared by diluting 118 ml of pure

acetyl chloride to 1 litre with dry toluene. Ten millilitres of this reagent were cooled to 10°C and two millilitres pyridine were added. The solution was shaken, 25.0 ml acetone added, and allowed to stand after further shaking for three minutes. One millilitre of absolute alcohol was added, the solution was allowed to stand for six minutes; all operations being performed in the dry box. A further 25.0 ml of alcohol were added and the solution shaken. After standing for 10 minutes the solution was titrated with the standard alkali using phenolphthalein indicator. A blank titre was obtained by following the above procedure but omitting the 25ml of acetone under test. The results for the acetone with less than 0.005% water were quite unsatisfactory, varying from 0.0 to 0.1%. The reason is probably because the difference between sample and blank titres was too small to give accurate results i.e. the precision of the method is above 0.005% water. Even using 50 ml. acetone did not improve the results. The method was tried as no detection limit was mentioned in the publication.⁴¹

2.5 Using Calcium Hydride.

Coetzee and Siao⁴² mention moisture determination in acetone involving measurement of the volume of hydrogen evolved by calcium hydride, correcting for reaction of the hydride with acetone itself. Details were not given and this approach was not attempted.

2.6 Conclusions.

It is apparent that determination of water in acetone below about 0.005% presents rather special problems. Methods suitable for moisture contents above this value are, in general, not accurate or precise

enough at very low moisture levels.

For acetone with moisture contents of the order of 0.005% or less, the Karl Fischer titration methods give the most accurate and precise results.

The results indicated a satisfactorily low moisture content which remained constant throughout the work, and which can best be determined by Karl Fischer titration using either modified reagent with the electrometrically determined end point.

However, it seems possible that extension of infra-red methods to enable accurate determination of low moisture contents in acetone will provide a simpler, more rapid and less tedious procedure. An infra-red method would also avoid the necessity of preparing and using the modified special reagent which, probably due to its pyridine content, was found to be most unpleasant and possibly presented a health hazard.

PART III.

CONDUCTANCE OF PERCHLORATES, PERCHLORIC ACID AND LITHIUM CHLORIDE IN ANHYDROUS ACETONE BY THE FOUR-ELECTRODE A.C. POTENTIOMETRIC METHOD.

III.1 Introduction.

A survey of the literature reveals that conductances of solutions of perchloric acid and some of its salts in acetone were determined by Ross Kane;⁹ and of the alkali perchlorates by Accascina and Schiavo.¹¹ Ross Kane found them to be fairly strong electrolytes and the latter authors weak electrolytes. However, Ross Kane never published his results in detail. His perchloric acid solutions were prepared by passing excess hydrogen chloride into a solution of silver perchlorate in acetone, precipitating silver chloride and using the decanted liquid as stock solution. He obtained a value of $207 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ for the limiting conductance of perchloric acid in acetone from an extrapolated plot of Λ against \sqrt{c} . It seems probable that his solutions contained constituents other than perchloric acid and acetone, and Kraus⁸ suggests that his acetone was of inferior quality. Ross Kane⁹ also expected a high error in his results due to difficulty in making the acid solutions.

While this conductance work was being completed a value of $\Lambda_0 = 205 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ for perchloric acid in acetone was published by Coetzee and McGuire.¹² They prepared solutions of 72% perchloric acid in acetic acid, removed the water by addition of acetic anhydride, diluted this solution with acetone and measured the conductance of the resulting solution. They assumed acetic acid was too

weak to affect the results and did not correct for its presence.

In this work the conductances of pure anhydrous perchloric acid in pure anhydrous acetone were measured by the four electrode A.C. potentiometric method to be described later (III.2.1.). A Fuoss⁴⁵ analysis gave a value of $214.0 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ for limiting equivalent conductance, some 3.4% greater than Ross Kane's value. Considering the experimental methods and extrapolation procedures he was forced to use it is, in fact, rather surprising that the difference is not larger. The conductance of ammonium perchlorate has never been measured in acetone before by any method.

It seemed possible that lithium chloride would prove a suitable salt for use in the transport number determinations (part IV) and as its conductance had not been determined previously, conductances for this salt were also measured. Recently¹⁴ a value of $\Lambda_0 = 214 \pm 4 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ * for lithium chloride in acetone has been published, somewhat higher than the value of 202.1 of this work. Further discussion of this point will be postponed until part III.6. All previous conductances were obtained with the two electrode method using platinised electrodes.

III.2 Apparatus.

2.1 The Four-Electrode A.C. Potentiometric Method of Conductance Measurements.

Conventional two-electrode A.C. conductance measurements are often in some degree liable to errors due to polarisation effects¹⁷ or the presence of platinised electrodes. For example, Kraus^{21,22} found

* Throughout this thesis conductances are in $\text{cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ unless otherwise stated.

adsorption errors in organic solvents, for which it is better to use unplatinised electrodes.

Bright platinum electrodes have been used in the well-known direct current conductance method,¹⁰ but besides being limited to cases where reversible electrodes are available, some workers have experienced difficulty in using this method for non-aqueous solvents. For example Gordon and co-workers,⁴⁶ working with ethanol, had to avoid prolonged passage of current through the probe electrodes as a result of any 'off-balance' in their initial potentiometer setting. Also they were unable to measure solvent conductance by the direct current method. No such difficulties or any other untoward effects have been experienced with the bright platinum four electrode alternating current potentiometric method used in this work.

In 1957, a prototype instrument for measuring electrolyte conductance using bright platinum electrodes was developed in co-operation with this laboratory,²³ based on that originally published by Wenner¹²¹ for measuring resistivity in geophysical prospecting work. The prototype was unsuitable for measurement of high resistances, which precluded work with acetone solutions. The prototype instrument has since been redesigned and a new instrument, specially adapted for conductance measurements in dilute solutions, was used in this work. The instrument was built by the Instrument Manufacturing Corporation of S.A. Ltd.. Tests, similar to those performed on the prototype,¹⁶ were made to determine the frequency

dependence and suitability of this instrument (III. 2.6).

The principles involved are illustrated in fig. 4. The four electrode cell contains two outer current electrodes, C_1 and C_2 , immersed in the solution the conductance of which is to be determined. A small current at 1 kc/s is passed between C_1 and C_2 . The potential difference between two probe electrodes is measured by balancing it against a voltage derived from a potentiometer R. The conductivity is proportional to the ratio of the current between C_1 and C_2 and the potential difference between P_1 and P_2 , and this ratio may be measured from the null setting of R by deriving the potentiometer supply voltage from a transformer TC placed in the current supply circuit.

/2. 2

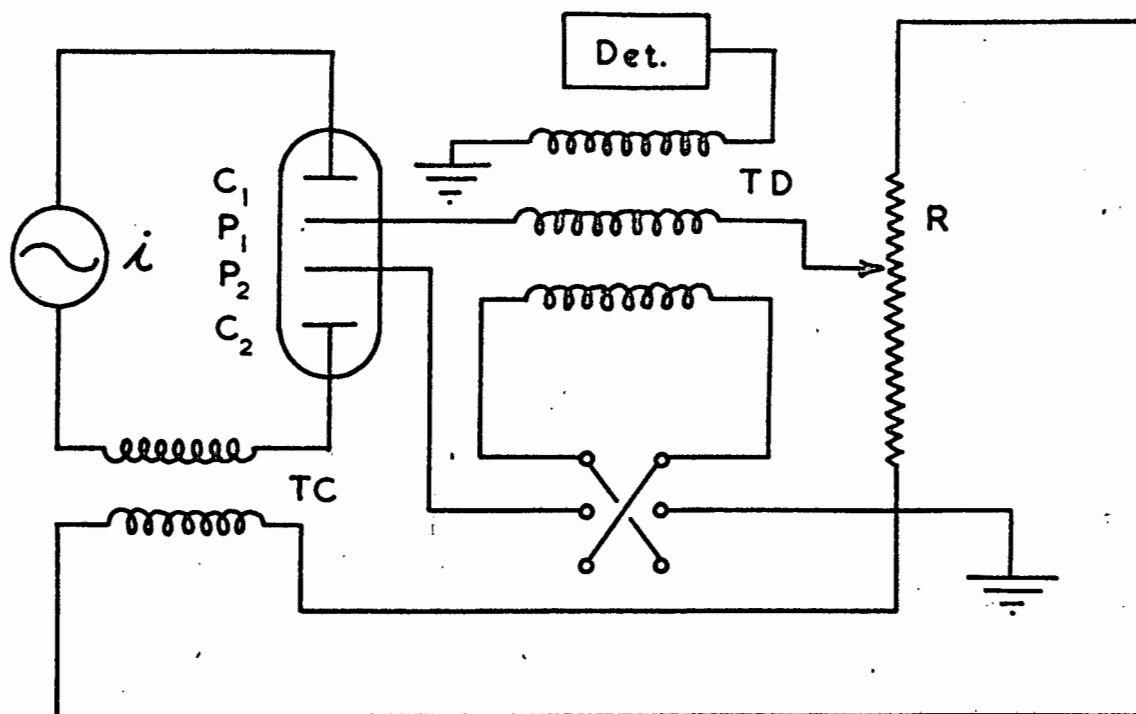


Fig. 4. Fundamental circuit

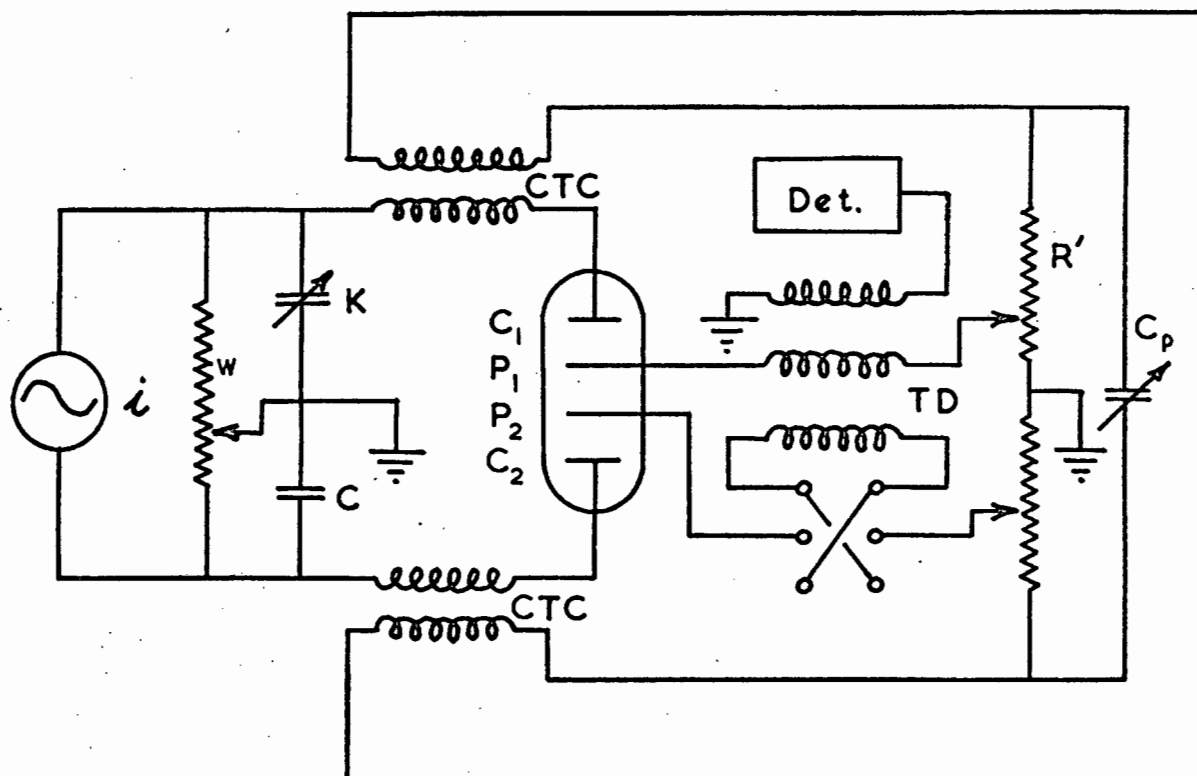


Fig. 5. Detailed circuit

2.2 The Transformer, Potentiometer, Oscillator and Detector.

The quality of the transformer TC must be such that, over wide variations in the primary current due, for example, to oscillator design or variation of contact resistance at the current electrodes, the secondary voltage remains directly proportional to the current i.e. the transformer ratio must remain constant even when the current through the cell varies.

Since at balance the potential difference across $P_1 P_2$ is accurately balanced against a potential supplied by R, no current flows in P_1 and P_2 , and hence the measurement is independent of the contact resistance of the probe electrodes. The balance condition is detected by summing the currents flowing from electrodes P_1 and P_2 in two primary windings of a detector transformer TD. A false null balance may be obtained if these currents are equal in amplitude and phase, and to guard against this the connections to one winding are reversed and adjustment repeated until balance is obtained.

Small circulating currents, which arise from interwinding and other stray capacitances, such as those to ground from the potential electrodes, pass through the probe electrodes and produce contact resistances. These currents and small phase shifts in the current transformer, TC, result in false null balances on the detector, and require the use of the more elaborate circuit of fig. 5 in order to balance out their effects. A double current transformer, CTC, and double potentiometer, R' , the centre point of which is earthed, are employed. The whole system is made symmetrical with respect to resistance by adjusting the variable resistance W, the variable capacity K being used to obtain symmetry with respect to capacitance. The current transformer introduces a small

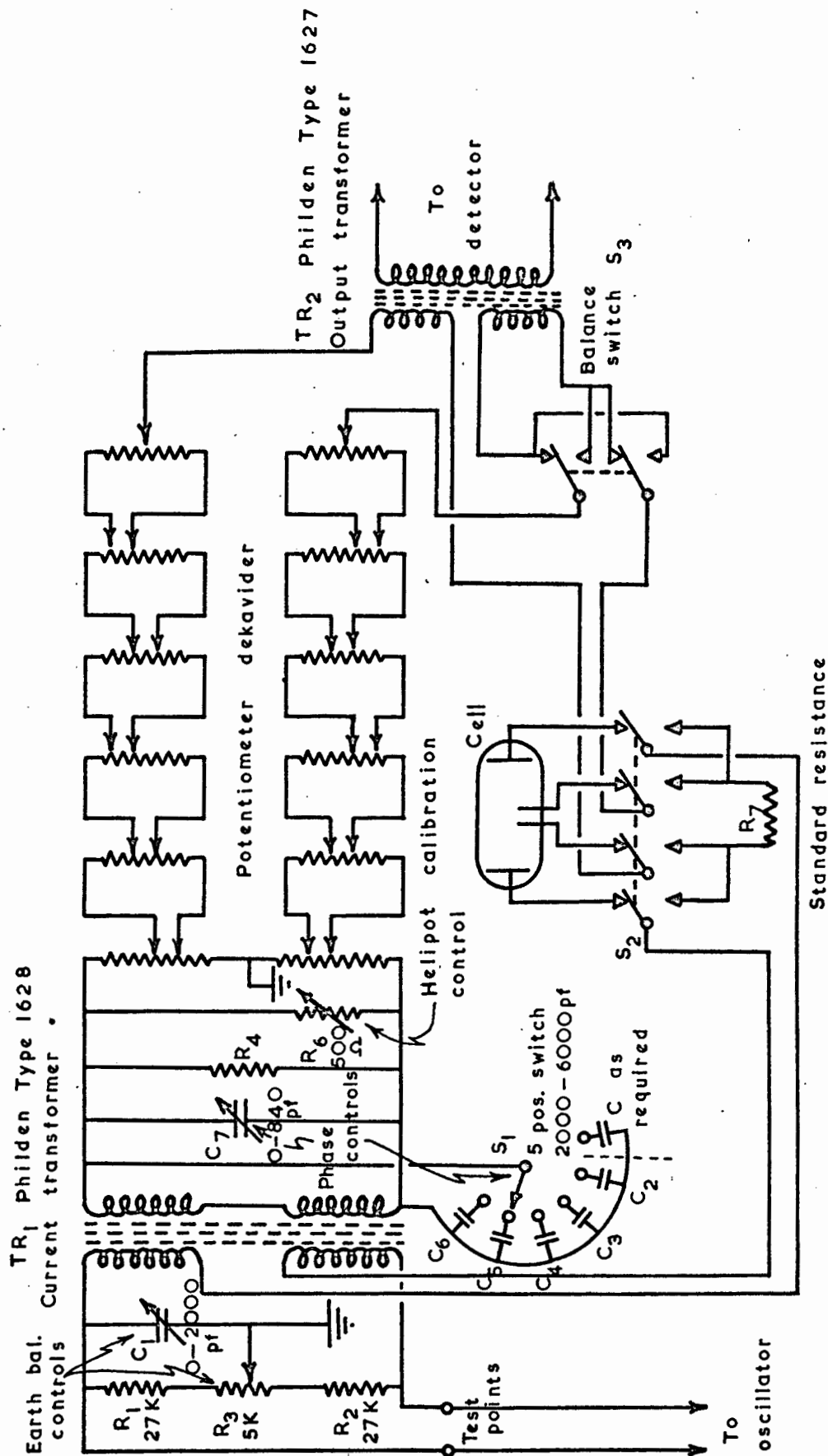


Fig. 6. Potentiometer circuit diagram

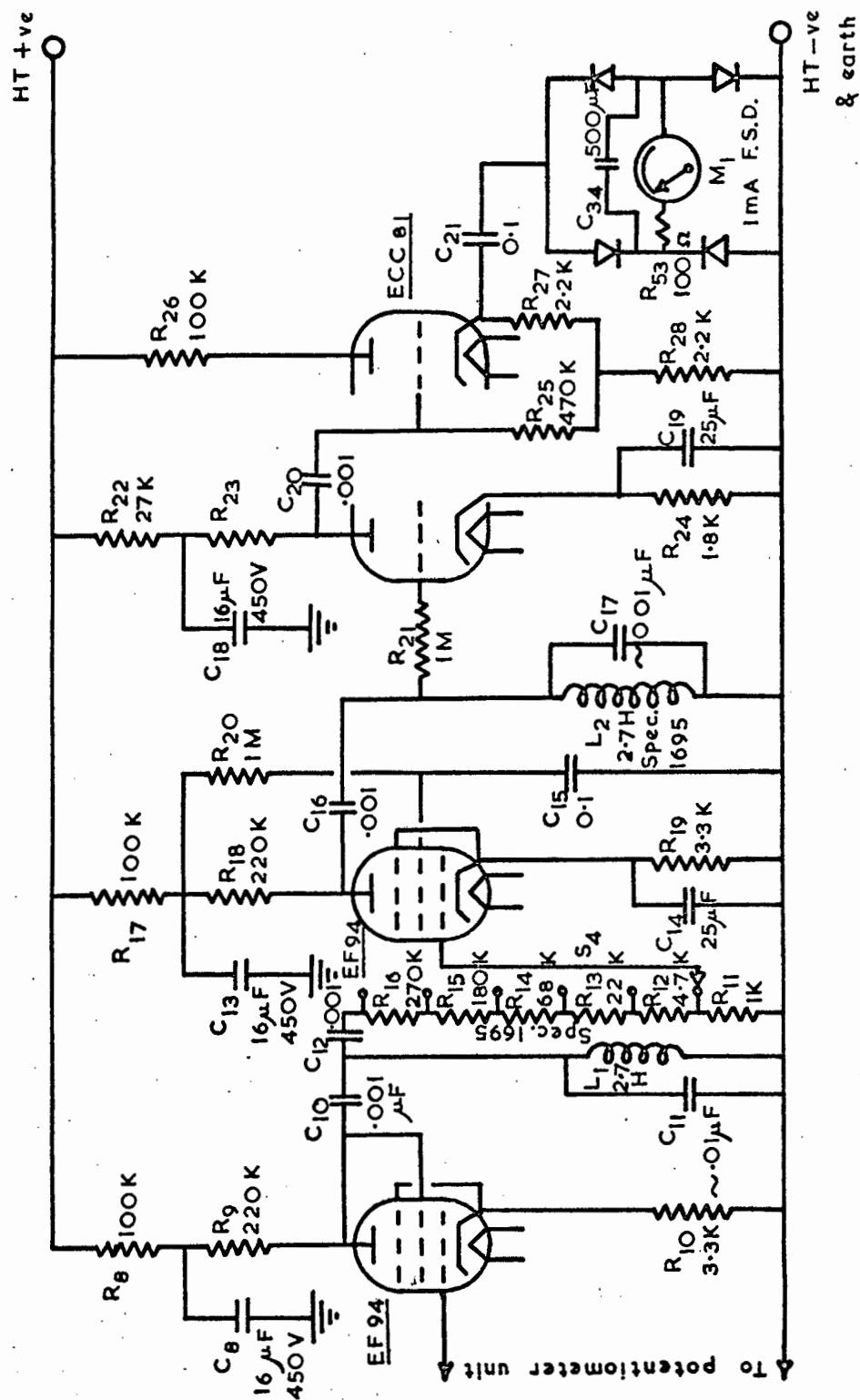


Fig. 7. 1000 c/s Detector

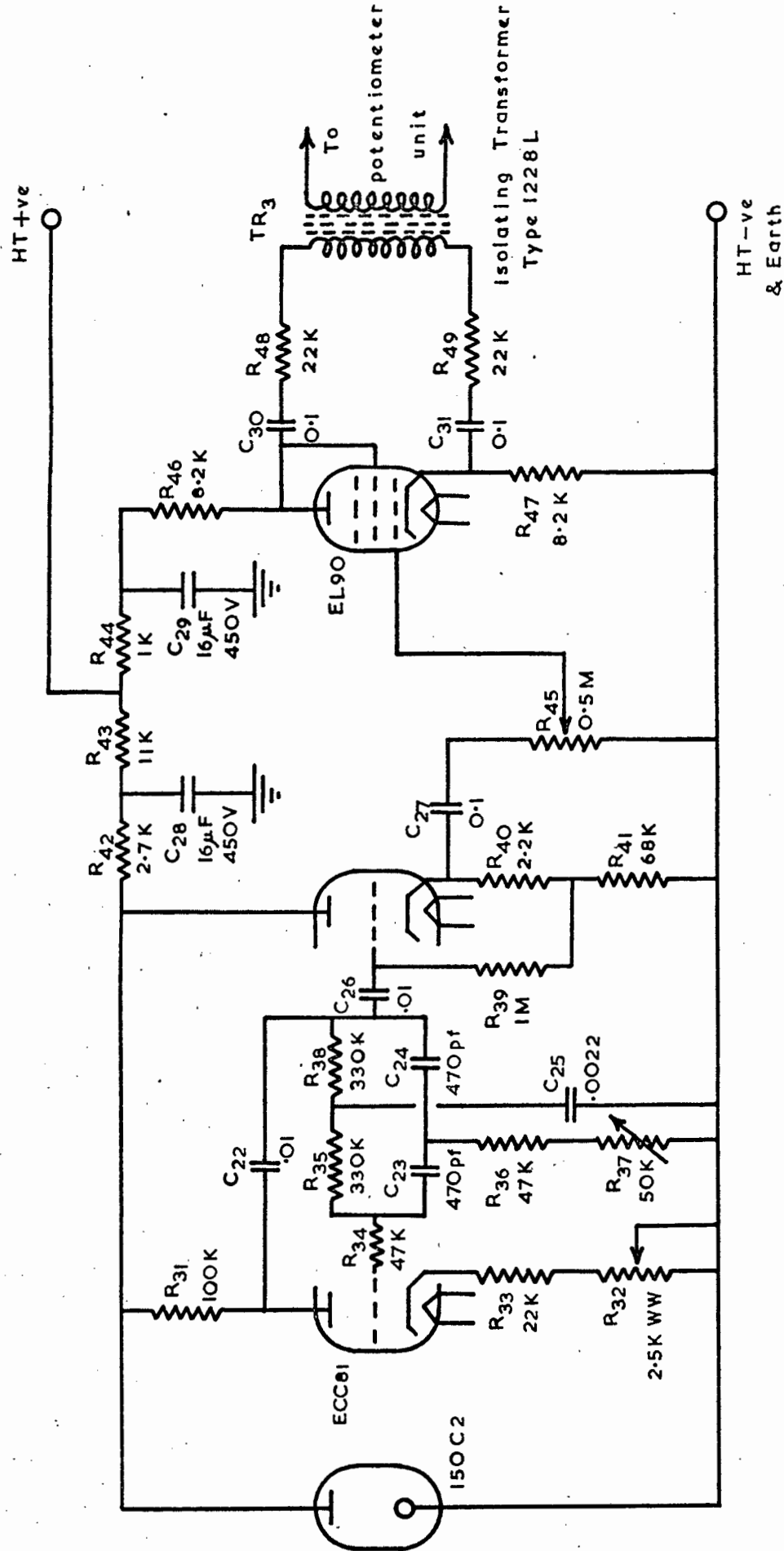


Fig. 8. Approximately 1000 c/s oscillator

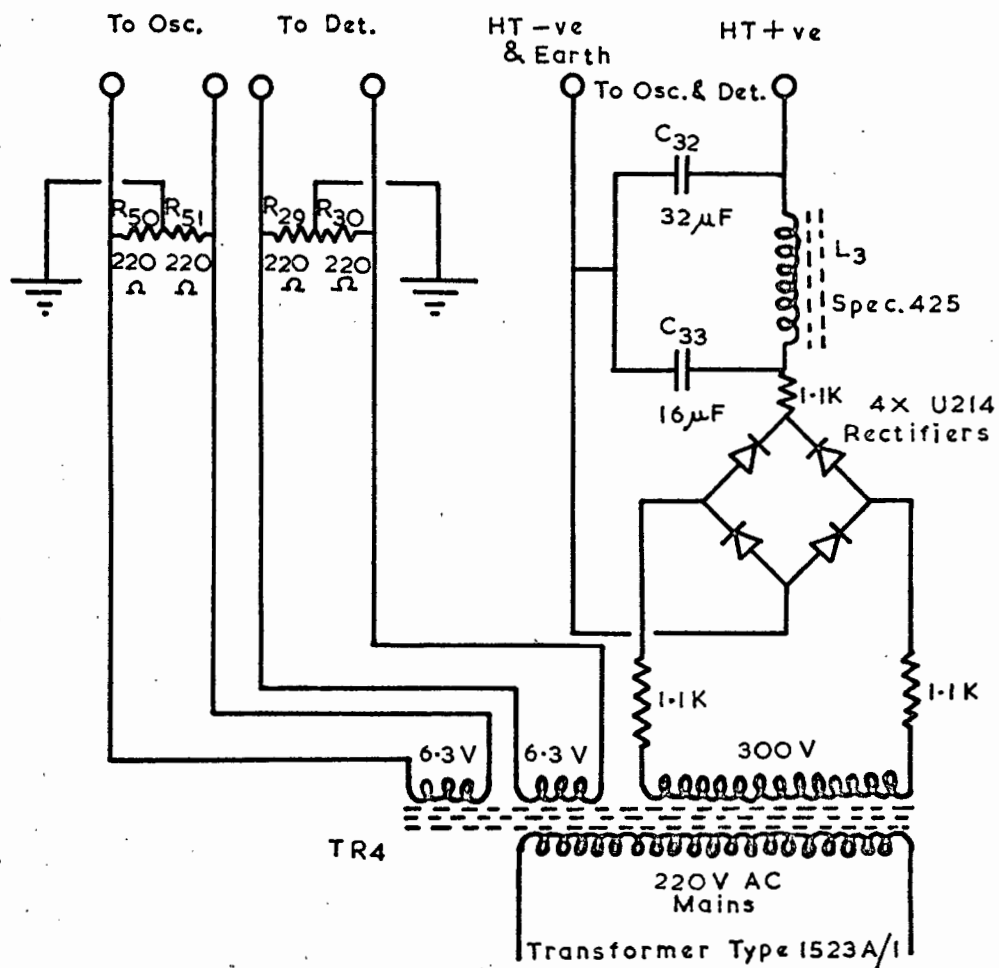


Fig. 9. Power pack for potentiometric measurements

but definite phase lead in the secondary voltage, and this is balanced out by the phasing capacitance C_p connected across the measuring potentiometer.

A reversing switch is used to connect the two primary windings of the detector coupling transformer, TD, in series adding or opposing. The potentiometer setting is adjusted in conjunction with the phasing and earth balancing controls until no current flows in the secondary of TD whatever the position of the reversing switch.

The full circuit diagrams of the potentiometer unit, null balance detector tuned to 1 kc/s, approximately 1 kc/s oscillator and the power pack used are shown in figures 6, 7, 8 and 9 respectively.

The potentiometer dekavider Type CA346 (fig. 6) is a double one, as shown, with a maximum resistance of about 6 K ohms. This is only a nominal figure, but the steps into which it is divided are very precisely equal. The linearity of the potentiometer is $\pm 0.001\%$. The maximum reading in scale divisions is 99,999 so that the linearity of the instrument is within ± 1 division. Hence, for a precision of 0.02%, the reading should not be less than 5,000 divisions. In practice it was found that readings on a particular solution could be determined with a precision of ± 2 divisions in general, and hence measurements were not made on solutions which required a potentiometer setting of less than roughly 10,000 divisions.

However, this instrument can be made to read full scale for any resistance up to the maximum value by adjusting the value of the

parallel resistor R_4 (fig. 6), which can be easily performed via connection terminals which are external to the chassis. For accurate work only high quality resistors can be used for R_4 . The calibration control, R_6 , a 500 ohm - 10 turn Helipot fitted with a duodial, (see III 2.5) has the same effect as R_4 , but a much smaller range.

Once R_4 was chosen (for most dilute solutions it was infinity i.e. R_4 was not connected) the instrument was calibrated by measuring the resistance at 25.00° of a Muirhead Type D333A 100.02 ohm N.P.L. certified standard resistor and Type A-60 999.95 and 2,999.7 ohm certified standard resistors. Since the linearity of the potentiometer was $\pm 0.001\%$, only one resistor would have sufficed, but three were used to confirm that zero resistance was within 1 division of zero. It will be noticed that the linearity of the potentiometer was far greater than the precision with which most conductance measurements can be made.

The leads from the potentiometer transformer TR1 (fig. 6) to the four electrode cell were shielded coaxial cables and the shields were earthed.

2.3 Thermostats.

The temperature was controlled using an oil thermostat placed inside an air thermostat.

The air thermostat was a cylindrical wooden drum kept at $23.0^\circ \pm 0.5^\circ$ by a Sunvic type TS3 bimetallic strip thermoregulator connected to a Sunvic type F102-3 relay. The air heater was a 40 watt electric light bulb in warm weather, and a 60 watt bulb in cold weather, the air being circulated by a fan driven by a small shielded electric motor mounted outside the drum. The regulator and relay were also

shielded and all shields were earthed to prevent possible interference with the conductance measurements by outside electrical changes.

The oil thermostat was a Buhler Superthermostat, containing Shell Diala B transformer oil, and had a capacity of 14 litres and a variable pumping rate of 2-10 l/min. The thermostat pump also acted as a stirrer, and the energy dissipated in pumping was sufficient to cause heating above 25° . Cooling water at $22.0^{\circ} \pm 0.1^{\circ}$, thermostatted using a Braun Thermomix 11, was run through cooling coils five metres in length inside the oil thermostat. The Buhler thermostat was equipped with a Perspex lid which had holes drilled in it for the necessary current and probe leads and thermometers. The leads were connected to the potentiometer via an Amphenol socket which was fastened to the side of the wooden air thermostat. A thermal equilibrium wire led from a screw holding the socket through the Perspex lid into a 5 ml flask of mercury submerged in the oil. This ensured that there was no temperature difference between the Amphenol socket with its attendant connections to the potentiometer unit and the conductance cell, which could have caused temperature changes in the cell due to thermal conduction along the current and probe leads.

In order to ensure maximum control by the thermostat, i.e. a heating phase slightly larger than the cooling phase, provision is made for fitting a resistor in series with the heating element. For this purpose a 250 ohm rheostat was used. Initial rapid heating was obtained by shorting out the rheostat and using the full 350 watt output of the heating element. Once the temperature of the oil had been raised to 25° the rheostat was adjusted to 250 ohms, thus reducing the heater

power to 60 watts.

The conductance cell, supported on a Perspex stand (III 2.4) was placed in a cylindrical thin walled polyvinyl chloride beaker 16 cm high and 18 cm diameter in which a few small holes were drilled. This beaker acted as a thermal 'buffer' to slight temperature fluctuations in the surrounding oil due to the operation of the Buhler thermostat control. The buffer vessel was washed on all sides by thermostat oil. The temperature in the thermostat was allowed to reach 25.00° before the buffer vessel was placed in the thermostat and filled with oil at 25.00° . This procedure enabled rapid attainment of thermal equilibrium.

Temperature could be controlled at 25.00° to within $\pm 0.005^{\circ}$. The temperature in the buffer vessel was read on a calibrated thermometer and temperature variation on a type F23 thermistor and Beckman thermometer.

2.4 The Four-Electrode Cells.

Two cells were used, the smaller for measurement of solutions with high conductances, the larger for solutions with lower conductances. The large cell, (I), (fig.11) consisted of two approximately circular plates of platinum about 6.3 cm in diameter set 1.6 cm apart. These current electrodes were set about 1.0 cm away from the Pyrex glass walls of the cell on stout platinum wires. The probe electrodes were platinum wires sealed between the current electrodes, projecting about 0.8 cm into the cell, and set about 0.3 cm apart. Electrical contact was made through mercury cups into which

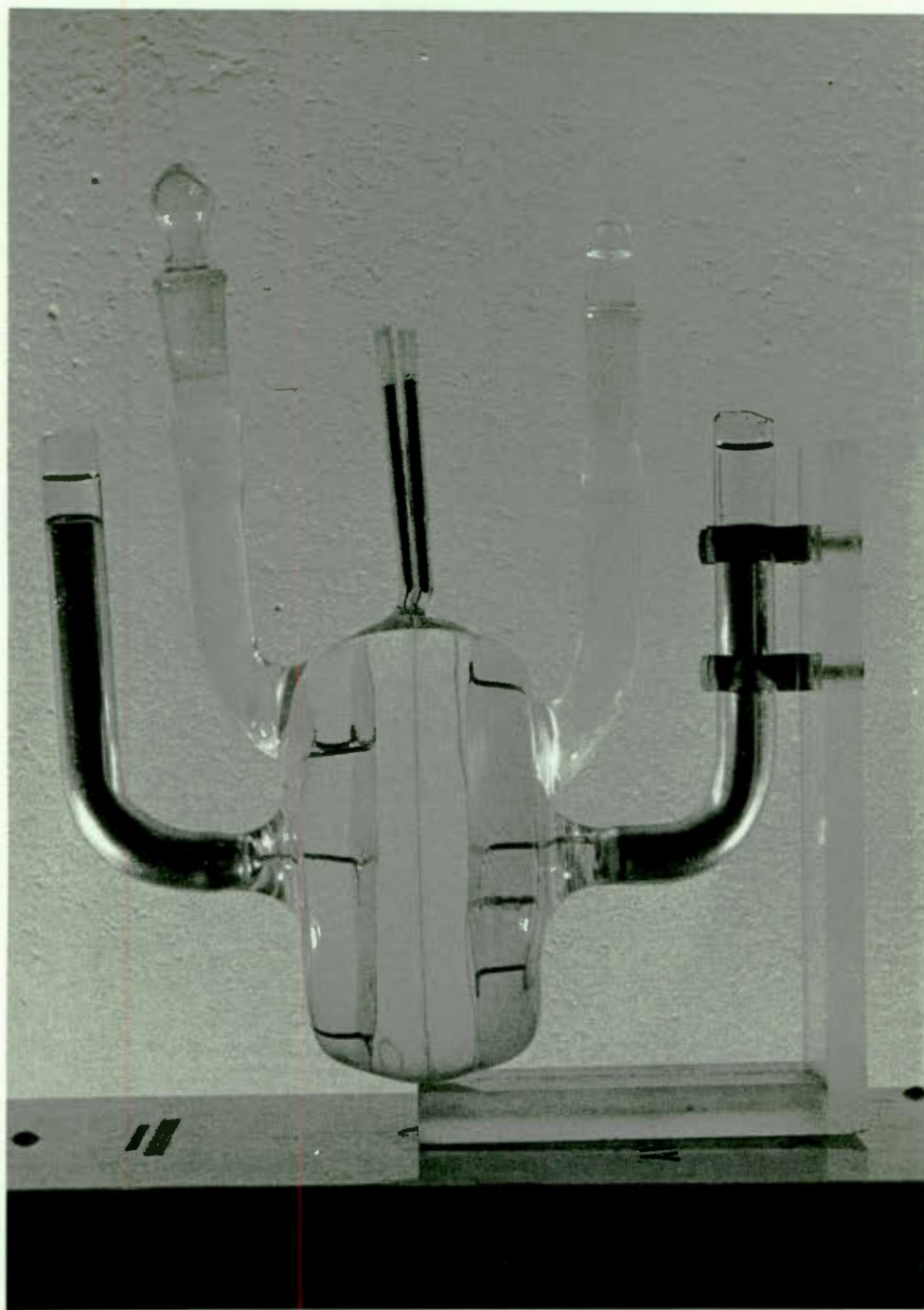


Fig. II. Conductance Cell.

dipped platinum wires spot-welded to the copper wires leading to the potentiometer. All wiring was as short as possible and its resistance was corrected for.

The smaller cell (II) was similar to the large one, except that the current electrodes were about 4 cm. diameter and 1.4 cm apart and the probes were set about 0.5 cm. apart.

The cells were mounted on specially designed Perspex stands (fig. II) and held in place by a tight-fitting clip. This simplified placement in the thermostat and manipulation in the dry box (III.4.1).

Current through the cells was kept as low as possible to minimize heating effects, and contact e.m.f's were avoided since alternating current was used. The cells were filled and sealed through B10 ground glass joints, with Polytetrafluoroethylene (P.T.F.E.) sleeves on the stoppers, which ensured airtight, moisture-proof seals.

It was found that changing from cell I to cell II introduced a different capacity and the capacitors, C_2 to C_6 , (fig. 6) became inadequate for balancing the out of phase component. The capacitance range was therefore extended as required, only good quality capacitors being used, as ordinary 'paper' ones have sufficient leakage to upset precision measurements.

The cell constants were determined with KCl solutions. The salt was Johnson and Matthey Specpure dried in a platinum dish for 6 hours at 200°C and cooled in a vacuum desiccator over silica-gel. Conductivity water was prepared by the method of Faure¹²⁵ for these tests and had a specific conductance of $6-8 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$

The solutions were made up by weight in volumetric flasks. The equation¹¹⁹ $C = 0.99707m - 0.0272m^2$ with m in moles/1000g solution was used to convert concentrations to molarity units at 25°C.

The conductivities of the solutions measured were calculated using the smoothing equation of Fuoss¹¹⁹ and co-workers which is based on Jones and Bradshaw's¹²⁰ values for the specific conductance of KCl solutions. The cell constants were measured at intervals during the work, seven measurements in all being made on each cell. The average values are shown below, the error being stated in terms of the range about the mean.

$$\text{Cell } \underline{\text{I}} : 0.0024593 \pm 7 \times 10^{-7} \text{ cm}^{-1}$$

$$\text{Cell } \underline{\text{II}} : 0.022357 \pm 5 \times 10^{-6} \text{ cm}^{-1}$$

When not in use the cells were stored filled with conductivity water, the electrodes connected by platinum and copper wires.

Tests with aqueous Specpure sodium chloride solutions over the concentration range 5×10^{-4} - 0.1 molar gave results agreeing with those of Shedlovsky¹²¹ to within 0.04% with $\Lambda_0 = 126.45$, thus indicating the equivalence of the potentiometric and conventional methods of conductance measurements. Unambiguous proof of this equivalence can only be obtained by an absolute determination of the conductance of aqueous potassium chloride by the potentiometric method.

2.5 Operation of the Potentiometer.

The short term accuracy of the conductivity measurements was maintained by checking against a standard wire-wound resistor, R_7 , built into the instrument (fig.6). Long term accuracy was maintained

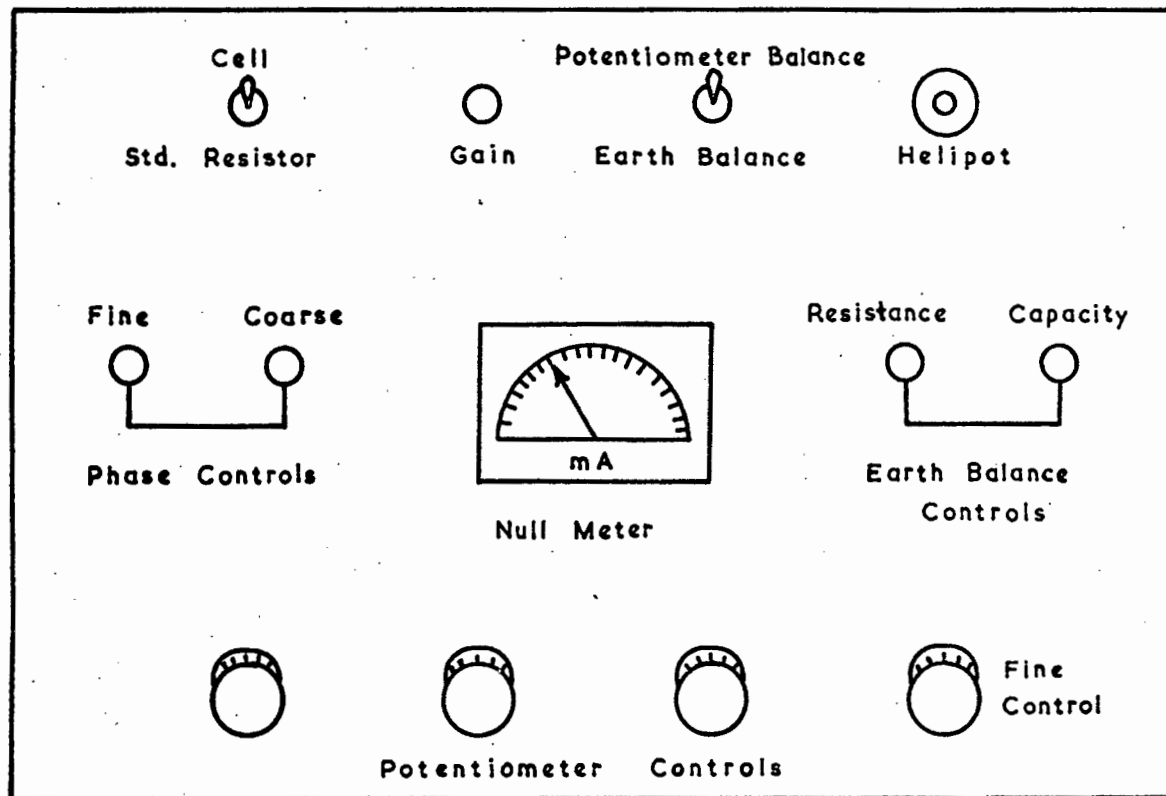


Fig. 10. Potentiometer Control Panel.

by checking daily against a Muirhead Type D333A 1K standard resistor with a negligible temperature coefficient.

In order to test if the potentiometer unit was functioning correctly (on a few occasions faults were found) the following procedure was adopted:

- 1.) All controls (fig. 10) were set to half-scale, except the gain control (fig. 7) which was set at a minimum.
- 2.) The internal standard resistor, R_7 , for checking short term accuracy, was switched in (switch S_2 , fig. 6).
- 3.) The balance switch, S_3 , was set on "Potentiometer Balance."

The null meter then read full scale i.e. off balance.

- 4.) The potentiometer reading was adjusted and the null meter dropped until it reached a minimum at some particular potentiometer reading, the fine control having no effect at this stage.
- 5.) The gain control was advanced and step 4. repeated until finally a minimum on the null meter was obtained.
- 6.) The "Phase Controls" were adjusted for minimum detector reading and a final setting was obtained by adjusting the potentiometer fine control and phase controls.
- 7.) With the gain a maximum, the null meter reading should be not more than $50 \mu A$. A change of 5 divisions of the potentiometer fine control (ca. 0.25 ohm) should bring the null meter to half scale (0.5 mA).
- 8.) The gain (S_4 , fig. 7) was reduced, the balance switch (S_3)

set on earth balance and "R" (resistance) and "C" (capacitance) controls (fig. 6) adjusted for a minimum detector reading with the gain eventually increased to maximum. If the above operations were successfully performed the instrument was functioning satisfactorily.

- 9.) The instrument was calibrated by switching to the test position marked "cell" (fig. 10) and measuring the external standard resistance (long term accuracy) mentioned in the sub-section (III.2.2) at 25.00° by adjusting the controls as indicated in steps 3 to 8 above. The relevant current and probe leads were connected to the standard resistor instead of a cell, the resistor being enclosed in a small glass container stoppered with a cork which held the electrical leads. The container was rendered leak proof by sealing with wax where necessary and was completely immersed in the thermostat oil at 25.00° .
- 10.) The internal standard resistance, R_7 (fig. 6), was switched in and the instrument balanced using the potentiometer and phase controls. Throughout the above procedures the Helipot control was kept locked at its midpoint (5 turns). The potentiometer reading was noted.

The instrument could now be re-calibrated during a series of measurements as follows:

11.)- With the gain control set at a minimum and the potentiometer reading set at the value found in step 10, the internal standard resistor, R_7 , was switched in and balance obtained using the phase and earth balance controls and the calibration Helipot control. The Helipot was then locked at its new setting.

For measuring cell resistances the cell was switched in (switch S_2) and the instrument balanced with the phase, earth balance and potentiometer controls.

In practice, after a two hour warm up, the instrument was calibrated at the beginning of a series of readings with the Helipot control set at its midpoint using the standard Muirhead resistor. The potentiometer reading for R_7 was obtained immediately afterwards.

Before a measurement was made the instrument was recalibrated against R_7 as in step 11. The above description shows that daily variations in the response of the instrument could be corrected by recalibration with the "long term" standard resistor. Short term fluctuations during a series of measurements, due possibly to variations in the ambient room temperature, could be corrected using the standard resistor R_7 .

2.6 Investigation of the Effect of Frequency Variation on Conductance Measurements.

In order to investigate whether frequency variation had any effect on the potentiometric measurement of conductance, the equivalent conductances of aqueous potassium chloride solutions were measured over the range 500 c/s to 8 kc/s.

The built-in fixed oscillator of ca. 1 kc/s was replaced by a Hewlett Packard wide range Model 200 CD oscillator. The output terminals of the Hewlett Packard instrument were connected through 0.1 μ F capacitors to the 22 k ohm resistors on the primary winding of the oscillator isolating transformer TR 3 (fig. 8). The output voltage from the test oscillator was adjusted to 0.6V at the test points shown on the potentiometer unit input (fig. 6). Two solutions of potassium chloride were prepared as described in III. 2.4, and their conductances measured in both cells. The conductances were calculated using the cell constants given in III. 2.4.

The results (table 3) show that any variation due to frequency change is within the limits of experimental error.

(TABLE 3)...

TABLE 3.

EQUIVALENT CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS
AT DIFFERENT FREQUENCIES.

KCl conc. mole l ⁻¹	Cell	Equivalent Conductance at Frequency				
		0.5 kc/s	1.0 kc/s	2.0 kc/s	4.0 kc/s	8.0 kc/s
0.009765	<u>I</u>	139.62	139.62	139.62	139.61	139.60
0.009765	<u>II</u>	139.63	139.62	139.62	139.62	139.61
0.0004612	<u>I</u>	147.08	147.09	147.09	147.08	147.08
0.0004612	<u>II</u>	147.08	147.09	147.09	147.09	147.07

N.B. Frequencies are given as read on the oscillator.

III.3 The Preparation and Purification of the Salts and Acid.

3.1 The Salts.

3.1.1 Sodium, Potassium and Ammonium Perchlorates.

B.D.H. laboratory reagent grade potassium and ammonium perchlorates were each recrystallised six times from conductivity water. The salts were dried in vacuo for 32 hours at 110° and cooled and stored in a vacuum desiccator over silica gel and phosphorus pentoxide. Great care was taken throughout the experimental work to ensure that all salts were kept dry. All manipulation of the salts during preparation of the solutions was carried out under dry nitrogen. (III.4.1).

Anhydrous sodium perchlorate was prepared by recrystallising B.D.H. laboratory grade hydrated sodium perchlorate from water at 55° - 60°, and the anhydrous salt was then recrystallised four times

from A.R. butanol, washed well with dry ether, dried at 250° for 26 hours and cooled and stored in a vacuum desiccator over silica gel and phosphorus pentoxide.

3.1.2 Lithium Perchlorate.

B.D.H. laboratory reagent grade 97% pure anhydrous lithium perchlorate, which was at the time a new addition to their range, was recrystallised three times from conductivity water and dried at 220° . The salt obtained from the recrystallisation, $\text{LiClO}_4 \cdot 3 \text{H}_2\text{O}$, loses two water molecules at 100° and the anhydrous product which is obtained at 149° melts at 236° and explodes at 368° .¹²³ 0.09427g of the resulting salt obtained was found to be insoluble in 50 ml of anhydrous acetone and only slightly soluble in ether and alcohol as judged by inspection. These findings are in complete contradiction to measurements by Willard and Smith,¹²² who found anhydrous lithium perchlorate to be very soluble in the above solvents. For example, they report the solubility of lithium perchlorate in acetone at 25° as 76.38g/100cc. Although these solubilities were not checked for accuracy, it appeared that the commercial salt obtained, apparently insoluble in several solvents, was unsatisfactory. The literature supplied by B.D.H. also mentioned the solubility in these solvents. Direct communication with B.D.H. resulted in the author's findings being confirmed, although no explanation has been found.

In general, the purification of salts is greatly simplified if reactants and solvents used in their preparation are carefully purified before use. Lithium perchlorate was therefore prepared from

Riedel de Haen A.R. perchloric acid and reagent grade lithium carbonate recrystallised from conductivity water by Booth's method which depends on the greater solubility of the salt in cold water than in hot water. Five such recrystallisations were performed and the salt dried in a drying gun at 110° in vacuo over phosphorus pentoxide.

Slightly more than the theoretical amount of 60% A.R. perchloric acid was added to about 20g of the pure carbonate in a platinum dish. The solution was then evaporated at the temperatures and for the periods suggested by Richards and Willard,²¹ until it solidified on cooling. Explosion screens were used and other precautionary measures taken when handling anhydrous perchloric acid which is highly explosive (see III. 3.2). The white crystals of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ obtained were filtered off, recrystallised three times from conductivity water, fused at 236° in a platinum crucible and the anhydrous perchlorate, m.p. $235.8 - 236.1^{\circ}$ was stored in a vacuum desiccator over silica gel and phosphorus pentoxide.

The anhydrous lithium perchlorate prepared as described above was soluble in acetone, but infra-red spectra of this sample and a recrystallised sample of the B.D.H. product showed no marked differences over the range $650 - 3,650 \text{ cm}^{-1}$.

3.1.3 Lithium Chloride.

Lithium carbonate, purified as described previously, was dissolved in A.R. concentrated hydrochloric acid, and the chloride which crystallised out was recrystallised three times from conductivity

water acidified with HCl and dried at 350° for 3 days, and then at 150° for two days in vacuo over phosphorus pentoxide. It was stored in a vacuum desiccator over silica gel and phosphorus pentoxide.

3.2 Anhydrous Perchloric Acid.

Ross Kane⁹ and Coetzee and McGuire¹² prepared their solutions of perchloric acid in acetone by chemical reactions. Ross Kane passed excess hydrogen chloride gas into a solution of silver perchlorate in acetone, precipitating silver chloride and using the decanted liquid as his stock solution of anhydrous acid in acetone. Coetzee and McGuire prepared a molar solution of perchloric acid in acetic acid by heating 71% aqueous HClO_4 in glacial acetic acid with the amount of acetic anhydride required to remove the water present. Dilute solutions in acetone were prepared by addition of the required quantity of acetone to this molar solution.

In this work pure anhydrous perchloric acid was prepared and dissolved in pure anhydrous acetone. 72% perchloric acid was dehydrated by the method of Smith¹²⁴ which involves vacuum distillation of 72% perchloric acid using anhydrous magnesium perchlorate as desiccant. The apparatus has been described by Sadie¹³ and is essentially a scaled down version of Smith's apparatus suitable for preparing 1 gram quantities of anhydrous acid. It is pertinent to mention here the precautions taken in this preparation. The entire apparatus was behind explosion screens and retort stands were screwed down to the bench. The experimenter should wear protective clothing such as goggles, a large mask and a

leather apron. Anhydrous perchloric acid explodes on contact with organic matter and for this reason ground glass joints were lubricated with a drop of 72% perchloric acid.

In order to show that the acid collected was anhydrous, Smith's method was used. Pure oxonium perchlorate, a white solid which melts at 49.9° , may be prepared by addition of 64.29g of 72% perchloric acid to 54.17g of the anhydrous acid. A white solid which melted at $49.8 - 49.9^{\circ}$ was obtained by addition of 0.27g of the distillate to 0.32g of 72% perchloric acid, thus showing the acid prepared to be anhydrous.

4. Conductance Measurements in Anhydrous Acetone by the Four Electrode A.C. Potentiometric Method.

4.1 General Procedure.

Throughout the experimental work described in this thesis all manipulations involving anhydrous acetone or dried salts and acids were carried out in the dry box, and great care was taken at all times to prevent any ingress of moisture. This care was taken even with non-hygroscopic salts and it considerably lengthened the period of experimental work, but ensured, as far as possible, the avoidance of errors due to the presence of water.

Where possible, all glassware was dried for several hours at 120° immediately before use. This included the flasks in which the acetone was refluxed and distilled (Section II.1) as well as 'volumetric' flasks used for preparing solutions by weight.

Glass apparatus was cleaned by soaking in a cleaning mixture of fuming nitric and sulphuric acids,⁴³ rinsing thoroughly with distilled water and then steaming the apparatus (beakers, flasks, etc.) in a 'steam bath' for several hours⁴⁴ before rinsing with conductivity water, oven drying and cooling in a stream of dry nitrogen. The use of the aforementioned cleaning mixture is preferred to the more conventional chromic acid which could leave chromium, and possibly other ions, adsorbed on the glass walls which may later desorb.

The conductivity cells were cleaned as described above when first made, but they were never heated once the cell constants had been determined. They were stored filled with conductivity water and periodically soaked in the acid cleaning mixture mentioned above for short periods followed by thorough rinsing with distilled and conductivity water. Before use they were dried with dry nitrogen and placed in the dry box on their stands (III 2. 4).

The general procedure for a typical run will be explained below; any deviations from this will be mentioned in the relevant sub-sections which follow.

Samples of salt in a stoppered weighing tube were weighed, transferred to a tared flask in the dry box and the tube reweighed. Future workers are recommended to carry out all weighings under dry nitrogen inside a dry box, thus reducing the time wastage involved using the above procedure. The flask was made up to volume (often 100 ml of stock solution) with anhydrous acetone and reweighed.

Subsequent dilutions, of which not more than two were made, were also performed by weight, the concentrations of the final solutions used being calculated on a molarity basis assuming the density of the solutions to be that of the solvent as is usual in cases of low concentration.^{8,17} Sadie's value for the density, viz.
¹³
0.7844 g/ml, was used.

The nitrogen-flushed conductivity cell was filled with solution, closed with ground glass BlO stoppers fitted with P.T.F.E. sleeves, removed from the dry box and placed in the thermostat. The stoppers were shown to be air tight by inverting the cells filled with acetone and leaving inverted overnight. No acetone was lost. After about two to four hours in the thermostat the resistance between the probe electrodes was measured on the potentiometer (III. 2.5) and the solution left for a further $\frac{1}{2}$ hour. Readings were taken at half-hourly intervals until a constant reading was obtained. Rocking the cell between readings did not alter the resistance, which remained constant once thermal equilibrium was attained. The cell was removed from the thermostat, the oil adhering to the outside rinsed off with carbon tetrachloride, the contents discarded and the cell returned to the dry box.

After flushing the box with nitrogen, another sample of the same solution was used to rinse the cell, and the cell was then filled with the same solution again. The resistance was measured as before and if it did not agree satisfactorily with that previously measured, the readings for this particular concentration were ignored. All

conductances were corrected for solvent conductance.

The solutions of a particular salt were measured starting with the most dilute and working up to the most concentrated, so as to reduce possible contamination errors, if any. The procedure followed with perchloric acid will be described in sub-section III.4.5. Two separate stock solutions were made for each salt and thus two separate series of solutions were measured in each case. The results of the two series were found to be compatible for all salts except sodium perchlorate. The first results with this salt were obtained before the technique had been perfected, and a third series of measurements was found to be compatible with the second.

Equivalent conductances were calculated from the measurements, and the results analysed by the Fuoss procedure to give limiting equivalent conductances and dissociation constants (III. 6). Least squares analyses of Fuoss data were performed using an I.C.T. 1301 computer.

4.2 Lithium, Sodium and Potassium Perchlorates.

Sufficient salt was weighed to give a precision of better than 0.01%. Solutions were prepared as just described and conductances measured.

A noteworthy point concerns the solubility of potassium perchlorate in dry acetone. Willard and Smith¹²² determined the solubility of KClO_4 in acetone as 0.155g/100 ml of solution at 25°. In this work, at 25°, it was noticed that a solution containing

0.08g/100 ml could not be prepared in anhydrous acetone because the perchlorate would not all dissolve. The problem was not pursued further but indicates the importance of having completely pure acetone.

The above authors' acetone had a density of 0.7852g/ ml compared to 0.7844 for this work.

The results are shown in tables 4, 5, 6, and the corresponding Fuoss plots appear in figure 12. An example of the details of a calculation are given in table 5. The limiting equivalent conductances and dissociation constants obtained are grouped in table 7.

TABLE 4.

THE CONDUCTANCE OF LITHIUM PERCHLORATE IN ACETONE.

FUOSS PLOT DATA

$10^4 c.$ mole l^{-1}	Λ $cm^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$	$\frac{10^3 F(z)}{\Lambda}$	$\frac{10^2 c \Lambda f^{-2}}{F(z)}$
4.3926	133.01	7.0489	4.6486
6.9265	119.42	7.7469	6.3288
8.1835	114.35	8.0473	7.0517
9.7411	109.03	8.3894	7.8759
13.785	98.54	9.1631	9.7344
17.022	92.29	9.6994	11.033

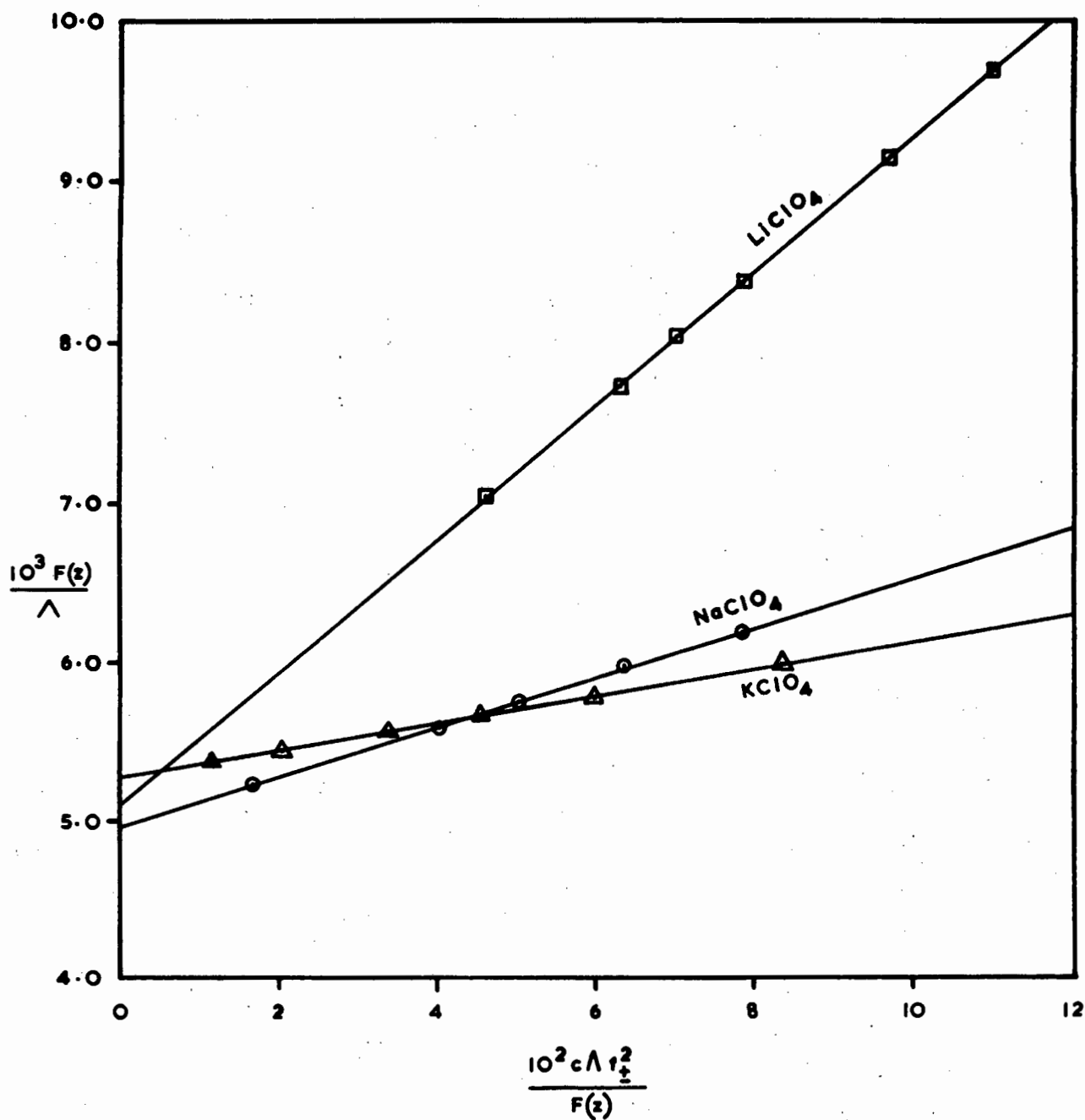


Fig.12. Fuoss Plots for Alkali Perchlorates.

TABLE 5.

FUOSS PLOT CALCULATIONS FOR SODIUM
PERCHLORATE

INITIAL $\Lambda_0 = 199.8$

$10^4 C$ mole l^{-1}	Λ $cm^2 ohm^{-1} equiv.^{-1}$	$F(z)$	f_{\pm}^2	$\frac{10^3 F(z)}{\Lambda}$	$\frac{10^2 C \Lambda f_{\pm}^2}{F(z)}$
1.0693	183.27	0.96364	0.8389	5.2581	1.7061
2.9778	168.28	0.94121	0.7568	5.6124	4.0229
4.0109	161.79	0.93271	0.7288	5.7730	5.0674
5.4610	154.18	0.92297	0.6981	5.9861	6.3801
7.3287	146.86	0.91241	0.6671	6.2128	7.8697

TABLE 6.

THE CONDUCTANCE OF POTASSIUM PERCHLORATE IN ACETONE

FUOSS PLOT DATA

$10^4 C$ mole l^{-1}	Λ $cm^2 ohm^{-1} equiv.^{-1}$	$\frac{10^3 F(z)}{\Lambda}$	$\frac{10^2 C \Lambda f_{\pm}^2}{F(z)}$
0.7311	180.07	5.3858	1.1565
1.3874	175.47	5.4648	2.0671
2.4653	169.52	5.5772	3.4027
3.5244	164.74	5.6799	4.5782
4.9259	159.43	5.7898	5.9812
7.6660	151.13	6.0142	8.3830

TABLE 7.

LIMITING EQUIVALENT CONDUCTANCES AND DISSOCIATION
CONSTANTS FOR THE ALKALI PERCHLORATES.

	LiClO_4	Na ClO_4	KClO_4
Λ_o	195.4	200.4	189.1
$10^4 K_D$	6.30	16.5	32.7

4.3 Ammonium Perchlorate.

Conductances were measured and analysed as for the other salts and the data and summarised calculations tabulated in table 8.

Figure 13 shows the corresponding Fuoss plot which results in a limiting equivalent conductance of $229.5 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$, with a dissociation constant of 7.24×10^{-3} .

TABLE 8 ...

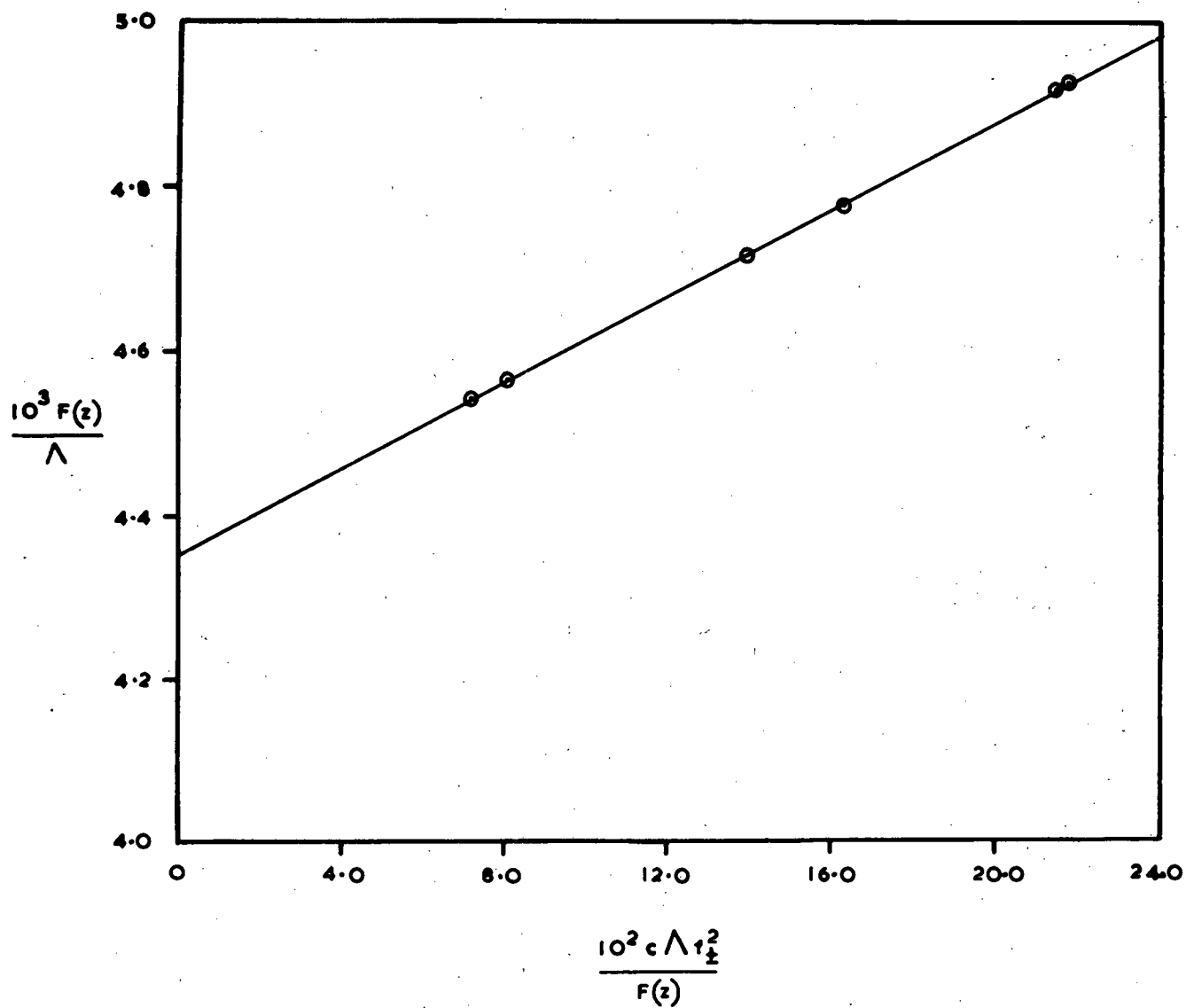


Fig. 13. Fuoss Plot for Ammonium Perchlorate.

TABLE 8.

THE CONDUCTANCE OF AMMONIUM PERCHLORATE IN ACETONE.

FUOSS PLOT DATA

$10^4 c$ mole l^{-1}	Λ $cm^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$	$\frac{10^3 F(z)}{\Lambda}$	$\frac{10^2 c \Lambda f_{\pm}^2}{F(z)}$
4.6443	204.98	4.5456	7.1856
5.3926	202.85	4.5687	8.0867
10.926	189.98	4.7233	13.984
13.883	184.97	4.7843	16.311
20.611	175.14	4.9210	21.525
21.359	174.36	4.9296	21.853

4.4 Lithium Chloride.

Conductances of this very hygroscopic salt were measured and analysed as for the other salts and the data and Fuoss plot are shown in Table 9 and figure 14. respectively. The equivalent conductance obtained is $202.1 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ with the very low dissociation constant of 2.9×10^{-6} .

TABLE 9 ...

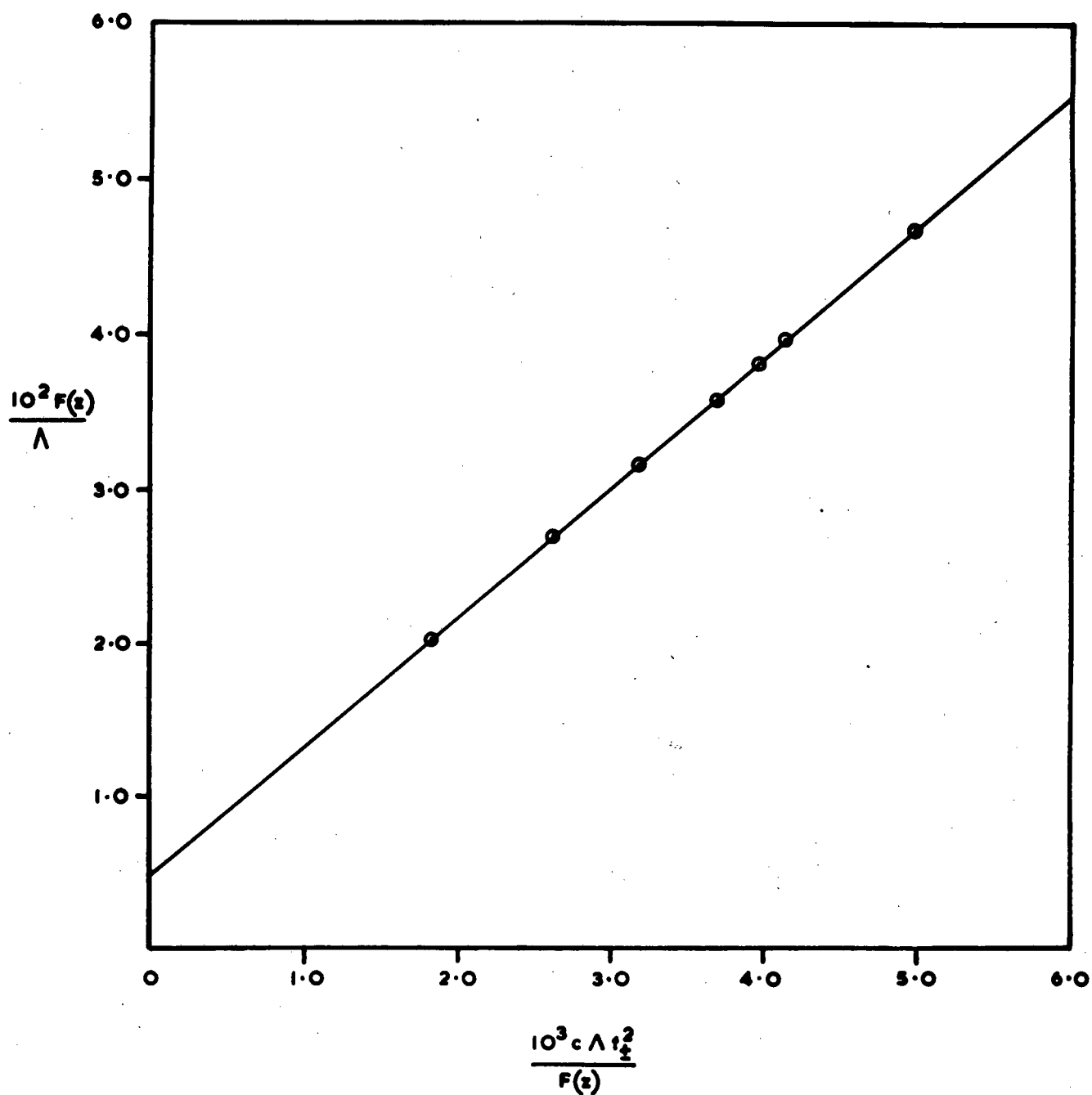


Fig. 14. Fuoss Plot for Lithium Chloride

TABLE 9.THE CONDUCTANCE OF LITHIUM CHLORIDE IN ACETONE.FUOSS PLOT DATA

$10^4 C$ mole l^{-1}	Λ $cm^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$	$10^2 \frac{F(z)}{\Lambda}$	$10^3 \frac{C \Lambda f_{\pm}^2}{F(z)}$
0.3532	48.38(3)	2.0462	1.8377
0.6700	36.52(7)	2.7051	2.6180
0.9551	31.11(5)	3.1724	3.1717
1.2586	27.41(1)	3.5966	3.6741
1.4595	25.70(1)	3.8337	3.9549
1.5880	24.76(4)	3.9783	4.1262
2.2771	20.95(6)	4.6942	4.9742

4.5 Anhydrous Perchloric Acid.

Weighed samples of anhydrous perchloric acid prepared as described earlier (III3.2), were transferred to weighed volumetric flasks and up to two successive dilutions by weight rapidly prepared from the reweighed stock solution. It was found by Ross Kane⁹ and Sadie¹³ that solutions of perchloric acid in acetone are unstable. In this work the stock solutions, which were initially colourless, rapidly turned a pale yellow which darkened to brown and finally black within about two days. This phenomenon has also been observed by the above two authors, and Hotz¹⁶ (see Part V. 1) with hydrogen chloride solutions in acetone. Sadie¹³ has shown it to be due to condensation reactions of acetone with the acid as catalyst. The condensations proceed more rapidly with perchloric acid than

hydrochloric acid as catalyst as evidenced by the rate of colour change of the solutions.

These effects made it necessary to adopt a different procedure from that followed in measurements on the salts. In a preliminary series of experiments, the acid was dissolved in acetone at room temperature (23°C on the day of preparation). The stock solution rapidly turned yellow, some of the diluted solutions were pale yellow before they were used and the conductances were widely scattered. A modified procedure described below was therefore adopted.

The stock solutions were prepared by dissolving perchloric acid in acetone previously chilled at -10°C , and their concentrations not allowed to exceed 0.01 molar. This delayed the onset of yellow colouration sufficiently (about two hours) to enable the dilute solutions to be prepared. The conductance of the most concentrated of these was measured first, since the condensation reactions are slower at lower acid concentrations, and the conductance of only one sample was measured instead of two. After each measurement the conductance cell was rinsed very thoroughly with the next more dilute solution, in order to avoid contamination with the more concentrated solution previously used. Following this procedure, all measurements were completed without any apparent deterioration of the solutions as indicated by colour change or variation of resistance with time.

It was noted that solutions of concentration 1.01×10^{-4} molar or lower showed no yellow colour even after five days. It would appear

that such solutions deteriorate relatively slowly, but kinetic investigation of the early stages of the condensation in this system seems desirable.

Three separate batches of anhydrous perchloric acid were prepared over an extended period of some months and conductances measured as described above. The results are shown in Table 10 and the Fuoss plot in figure 15. The limiting equivalent conductance is $214.0 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ with a dissociation constant of 6.7×10^{-4} . The precision of the perchloric acid data is 0.2% as opposed to 0.06% to 0.14% for the salts.

TABLE 10.

THE CONDUCTANCE OF PERCHLORIC ACID IN ACETONE

FUOSS PLOT DATA

10^4 C mole l^{-1}	Λ $\text{cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$	$\frac{10^3 \text{ F}(z)}{\Lambda}$	$\frac{10^2 \text{ C } \Lambda \text{ f } +^2}{\text{F}(z)}$
0.2662	202.79	4.8476	0.5367
0.4211	198.95	4.9199	0.7588
0.5961	195.10	4.9983	0.9999
0.8564	188.81	5.1399	1.4350
1.0108	185.87	5.2082	1.6448
1.5735	176.86	5.4347	2.3409
1.7456	174.96	5.4825	2.4877
2.2910	168.18	5.6729	3.0729
2.5065	164.58	5.7870	3.4235

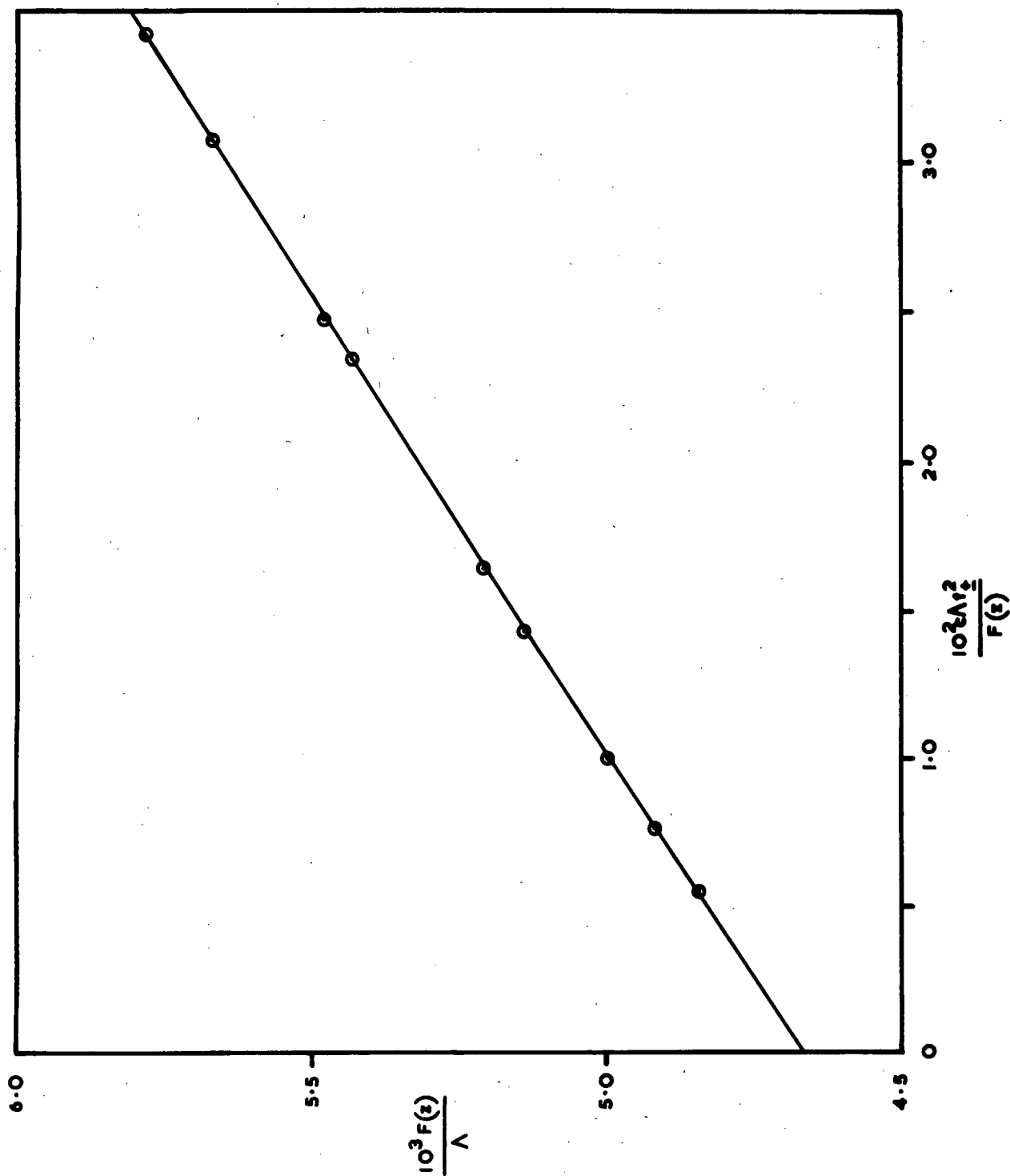


Fig. 15. Fuoss Plot for Perchloric Acid.

5. Theory of Electrolyte Conductance.

5.1 Introduction.

The properties of electrolyte solutions have been studied ever since Faraday's first experiments over a century ago. One of the first workable electrolyte theories was that of Arrhenius, which resulted in the familiar mass action equation

$$K = \frac{c\alpha^2}{1-\alpha} \quad \dots 5.1.1$$

where K is the equilibrium constant and $c\alpha$ the concentration of free ions. By Arrhenius' hypothesis $\alpha = \Lambda/\Lambda_0$ and combining these two equations gives the Ostwald dilution law

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + c\Lambda/K\Lambda_0^2 \quad \dots 5.1.2$$

However, strong electrolytes did not conform to the theory of Arrhenius. Debye and Hückel⁴⁸ in their treatment of the problem accounted for thermodynamic properties of electrolyte solutions, in particular giving the well-known limiting equation for the activity coefficient. They did not account for electrolyte conductance, this being left to Onsager.⁴⁹ His limiting equation can be written

$$\Lambda = \Lambda_0 - (\alpha' \Lambda_0 + \beta) \sqrt{c} \quad \dots 5.1.3$$

where α' and β are constants completely determined by the absolute temperature, T , relative permittivity, ϵ_r , viscosity η and universal constants, viz.

$$\alpha' = e^2 / 6\epsilon_r kT(1+q)^{\frac{1}{2}} \quad \text{and} \quad \beta = Fe\kappa/3\pi\eta C^{\frac{1}{2}} \times 10^{-8}.$$

where e is the electronic charge in e.s.u., k Boltzman's constant, F the Faraday, C the speed of light in vacuo, and $q = \frac{1}{2}$ for

symmetrical electrolytes.

κ is given by

$$\kappa^2 = \frac{4\pi N e^2}{10^3 k T \epsilon_r} \sum c_i z_i^2$$

where N is Avogadro's number, c the molarity and $z = 1$ for uni-univalent electrolytes.

Inserting the values of the universal constants as recommended by Fuoss⁴⁵ gives

$$\alpha' = \frac{0.8204 \times 10^6}{(\epsilon_r T)^{\frac{3}{2}}} \quad \text{and} \quad \beta = \frac{82.501}{\eta (\epsilon_r T)^{\frac{1}{2}}} \quad \dots 5.1.4$$

It must be clearly appreciated that Onsager's equation above, (5.1.3), is not the equation of a conductance curve but rather is the equation for the tangent to the curve at zero concentration. The limitation is the result of the assumption made by Onsager that the ions may be treated as dimensionless point charges. Bjerrum⁵² suggested that ions of strong electrolytes in solution could associate to non-conducting pairs (See III.6). Fuoss and Kraus⁵³ combined the Arrhenius, Debye-Hückel-Onsager and Bjerrum theories to give a preliminary form of a general conductance theory.

Fuoss and Onsager⁵⁰ made the next major advance when they took into account the finite sizes of the ions. The result was an equation of the form

$$\Lambda = \Lambda_0 - S c^{\frac{1}{2}} + E c \log c + J(a) c \quad \dots 5.1.5$$

where S is the Onsager coefficient of (5.1.3) and E is a constant defined by the variables T , ϵ_r and η . J is a function of ion size

parameter a . It should be noted that the presence of the logarithmic term makes it impossible to extrapolate conductance data as such to obtain limiting conductances by any algebraic expression. The above equation was derived for strong unassociated electrolytes.

Fuoss⁵¹ extended the above equation to the case of associated electrolytes, and obtained the equation

$$\Lambda = \Lambda_0 - S c^{\frac{1}{2}} \alpha^{\frac{1}{2}} + E c a \log c \alpha + J c \alpha - K_A c \alpha f^2 \Lambda \quad \dots 5. 1.6$$

where $(1 - \alpha)$ is the fraction of salt associated to pairs and is assumed to be related to K_A , the association constant, by the mass action equation modified to account for the long-range effects of Coulomb forces through the activity coefficient f .

$$1 - \alpha = K_A c \alpha^2 f^2 \quad \dots 5. 1.7$$

where f is the mean molar ionic activity coefficient computed by the Debye first approximation for ions of finite size

$$- \ln f = \frac{\beta' c^{\frac{1}{2}} \alpha^{\frac{1}{2}}}{1 + \kappa a \alpha} \quad \dots 5. 1.8$$

$$\text{or} \quad - \log_{10} f^2 = \frac{2 \beta'' c^{\frac{1}{2}} \alpha^{\frac{1}{2}}}{1 + \kappa a \alpha} \quad \dots 5. 1.8a$$

where $\kappa = 0.50294 \times 10^{10} \sqrt{c_0 / \sqrt{\epsilon_r T}}$ for uni-univalent electrolytes and $\beta'' = 1.8247 \times 10^6 / (\epsilon_r T)^{3/2}$ and a is the ion size parameter.

In these calculations an ion size parameter of 5 Å was used.

The final result is very insensitive to the a value used, but it

was felt that any reasonable value of a is better than assuming a is zero and using the limiting law.

At low concentrations 5. 1.8 is seen to be the familiar Debye-Hückel⁴⁸ limiting law

$$- \ln f = \beta' (c \alpha)^{\frac{1}{2}} \quad \dots 5. 1.9$$

which would also be obtained with $a = 0$ as mentioned earlier, i.e. if the ions were represented by point charges as in the original Onsager conductance theory. If the solution is so dilute that interionic collisions are rare, then the limiting law suffices.

Equation 5. 1.5 is based on the hypothesis that pairs of oppositely charged ions "in contact" would not conduct current.⁵¹ This ion-pairing occurs to an increasing extent for solvents of lower dielectric constant, such as acetone with $\epsilon_r = 20.47$ and equation 5. 1.6 must clearly reduce to 5. 1.5 as the association constant, K_A , approaches zero i.e. association tends to zero. Inspection of 5. 1.6 will show this to be so.

As mentioned earlier in this section the theoretical investigation of symmetrical electrolytes has been conducted using a model of rigid charged spheres in a hydrodynamic and electrostatic continuum. The ion-ion contact distances, a , calculated from $J(a)$ of 5. 1.5 or 5. 1.6 are found to increase for a given electrolyte as the dielectric constant of the solvent mixture decreases. Very recently Fuoss⁵⁴ has shown this to be a consequence of the model used and suggests that one including short-range

ion-solvent interactions will have to be considered to help overcome this failing. The most recent equation of Fuoss,⁵⁴ which is equivalent to 5. 1.6 when ion-pairing occurs, was derived theoretically without the artificial insertion of the mass action equation 5. 1.7, but use of this simplifies the derivation.

5.2 Choice of Conductance Equation.

When K_A is of the order of several hundred or larger, as in this work, the general conductance equation 5. 1.6 of the previous sub-section can be very much simplified,⁴⁵ since the sum of the terms in E and J becomes negligible compared to $K_A f^2 c \Lambda \alpha$, in other words the terms Jc and $Ec \log c$ approximately cancel each other. Also, over a small concentration range, the viscosity correction of the conductance due to the solute is negligible and 5. 1.6 becomes

$$\Lambda = \alpha (\Lambda_0 - S c^{\frac{1}{2}} \alpha^{\frac{1}{2}}) \quad \dots 5. 2.1$$

As an approximation the Arrhenius value $\alpha = \frac{\Lambda}{\Lambda_0}$ is used and substitution in 5. 2.1 gives the first approximation

$$\alpha_0 = \Lambda / \{ \Lambda_0 - (S / \Lambda_0^{\frac{1}{2}}) (c \Lambda)^{\frac{1}{2}} \}$$

A better approximation is then obtained by substituting α_0 for α giving

$$\alpha_1 = (\Lambda / \Lambda_0) \{ 1 - (S / \Lambda_0^{\frac{1}{2}}) (c \alpha_0)^{\frac{1}{2}} \}$$

Repetition of this process leads to the correct value of α which can be written as

$$\alpha = \frac{\Lambda}{\Lambda_0 F(z)} \quad \dots 5. 2.2$$

where
$$z = (S/\Lambda_o^{\frac{3}{2}})(c\Lambda)^{\frac{1}{2}} \quad \dots 5.2.3$$

and
$$F(z) = \frac{4}{3} \cos^2 \left\{ \frac{1}{3} \cos^{-1} \left(-3^{\frac{3}{2}} z/2 \right) \right\}$$

Values of $F(z)$ have been tabulated to facilitate calculation.⁵⁵

Substitution of 5.2.2 in the mass action equation 5.1.7

$$(1 - \alpha) c \alpha^2 f^2 = K_A \quad \dots 5.1.7$$

and rearrangement, gives

$$F(z)/\Lambda = \frac{1}{\Lambda_o} + c \Lambda f^2 K_A / \Lambda_o^2 F \quad \dots 5.2.4$$

Thus a plot of F/Λ against $C \Lambda f^2 / F$ will determine K_A / Λ_o^2 and $1/\Lambda_o$ as slope and intercept, whence K_A and Λ_o are obtained. Use of the method requires a preliminary value of Λ_o from which the independent variable z can be calculated by equation (5.2.3). Extrapolation of a Λ vs $c^{\frac{1}{2}}$ plot often gives a satisfactory initial Λ_o and after once extrapolating by means of 5.2.4, the value of Λ_o thus obtained is recycled to obtain more accurate Λ_o and K_A values.

This method of solution is valid below the concentration at which formation of triple ion clusters occurs. Fuoss⁴⁵ has stated this concentration to be $3.2 \times 10^{-7} \text{ } \epsilon^3$ which is $2.8 \times 10^{-3} \text{ mole litre}^{-1}$ for acetone. Ions will have physical stability when the magnitude of their interaction potential energy, $e^2/2a \epsilon_r$ is greater than the thermal energy kT . It should also be noted that the model used is not reliable at concentrations corresponding to $\kappa a > 0.02$, neglect of terms of order $C^{\frac{3}{2}}$ and higher in the

derivation of the equations resulting in appreciable errors at $\kappa a > 0.02$. For either of these two reasons concentrations above $\kappa a > 0.02$ are not to be used. Choosing $a = 5\text{\AA}$ gives

$$c_{\max} = 2 \times 10^{-4} \epsilon_r = 0.004 \text{ molar}$$

for uni-univalent electrolytes in acetone. This is higher than the limit mentioned above and thus the former limit is the relevant one in acetone for the equations used here.

It should also be noted that the present conductance equations⁴⁵ give Λ , as a first approximation, as a linear function of c and not $c^{\frac{1}{2}}$ as in the limiting law. Also the present conductance theory no longer makes it necessary to work at extreme dilutions as we no longer need to use a limiting law valid only at extreme dilutions.

Alternative methods of obtaining Λ_0 and K_A have been proposed by several authors including Shedlovsky,⁵⁶ Robinson and Stokes,⁵⁷ and the Falkenhagen school⁵⁸ and Ives.⁶⁰ They all have applications in certain special cases, none being superior to the Fuoss-Kraus-Onsager treatment. Shedlovsky's method is similar to that of Fuoss described above, and in the range of variables where either method may be applied they give almost identical results,⁵⁹ in particular for acetone with $\epsilon_r = 20.47$.

The values of the functions and constants used in the calculations for acetone at 25.00°C are shown in Table 11.

TABLE 11.

FUNCTIONS AND CONSTANTS FOR CONDUCTANCE CALCULATIONS.

Relative permittivity (dielectric constant), $\epsilon_r = 20.47$

Viscosity, $\eta = 0.00304$ poise.

$$S = \kappa \Lambda_o + \beta = 1.72058 \Lambda_o + 347.379$$

$$\kappa^2 = \frac{4 \pi N e^2 c}{10^3 k T \epsilon_r} \quad \kappa/c^{\frac{1}{2}} = 6.43778 \times 10^7$$

$$\beta'' = 0.4343 e^{2\kappa} / 2 \epsilon_r k T \sqrt{c} = 3.8269$$

$$-\log f^2 = 2\beta'' c^{\frac{1}{2}} \alpha^{\frac{1}{2}} / (1 + \kappa a \alpha^{\frac{1}{2}})$$

6. Discussion.

6.1 The Four-Electrode A.C. Potentiometric Method of Conductance Measurements.

This method, which has been described earlier (III. 2.1), enables conductances to be measured using A.C. current, in cells equipped with bright platinum, i.e. unplatinised, electrodes. Errors due to polarization effects are eliminated as no current flows in the probe electrodes at balance. At all concentrations used no shaking effect¹⁷ was observed. Prue and Sherrington,¹⁷ using the conventional two electrode A.C. method, found the shaking effect

in dimethyl formamide to be much less for bright platinum electrodes, but, as might be expected for polished electrodes with the two electrode method, polarization errors occurred at concentrations above 5×10^{-4} molar.

Polarisation errors can, in many cases, be partly or nearly completely avoided by platinising the electrodes. However, complete elimination of these errors requires perfect platinising - an unattainable ideal. Also, Kraus and co-workers^{21,22} found adsorption errors can arise under certain conditions such as when using large electrodes with platinum black coatings in the study of low ionic concentrations in organic solvents. The potentiometric method avoids the requirement of platinising the electrodes.

Certain reactions in solution are catalysed by the presence of finely divided platinum which renders accurate conductometric study of such solutions impossible when platinised electrodes are used.¹⁶ Clearly such effects are much less likely with the potentiometric method.

As described earlier (III.2) the conductance actually measured is of the solution between the probe electrodes, and hence errors due to 'end effects' at the current electrodes are obviated. Also, being a potentiometric method with no current flowing in the probe electrodes at the balance point, the state of the electrodes, which could give rise to contact resistances, is of no importance.

The advantage of all alternating current methods whereby contact

or thermal e.m.f.s. are avoided is, of course, retained.

6.2 Equivalent Conductances and Dissociation Constants.

The discussion of ion conductances and related subjects will be postponed until section IV, and discussion here will, in the main, be confined to conductances and dissociation constants.

In this work all the salts were found to have a considerable degree of ion pairing in acetone solutions, as was the case with perchloric acid which is, however, relatively strong compared to hydrochloric acid¹³ which has a dissociation constant of about 10^{-7} at 25° . Ross Kane⁹ also found perchloric acid to be relatively strong, although the solution he used probably contained impurities, as did Coetzee's.¹² Kraus⁸ considers all conductance work in acetone prior to 1948 to be suspect due to the large and uncertain solvent conductances found, and it appears that further consideration of Ross Kane's results, which were never published in detail, is not justified. Coetzee's conductance data for perchloric acid - acetic acid mixtures in acetone were published just after this work had been completed, but his data will not be considered further, because of the impurities present in his solutions. It should be noted that Coetzee's acetone was dried with phosphorus pentoxide, which reacts with acetone and is an unsuitable drying agent for this solvent.¹³

TABLE 12.
CONDUCTANCES IN ACETONE.

Electrolyte	Λ_o , $\text{cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$		Dissociation Constant, $10^4 K_D$	
	This work Potentiometric Method	Previous work Two Electrode Method	This work Potentiometric Method	Previous work Two Electrode Method
LiClO_4	195.4	187.3	6.3	1.9
NaClO_4	200.4	191.2 Ref ¹¹	16.5	2.3
KClO_4	189.1	188.7	32.7	1.4
NH_4ClO_4	229.5	-	72.4	-
LiCl	202.1	214 ¹⁴	0.029	0.033
HClO_4	214.0	-	6.7	-

Very recently¹⁴ conductance data for LiCl were published and this result, together with those of Accascina and Schiavo¹¹ for the alkali perchlorates and those of this work, are shown in table 12. All conductance work of previous workers was carried out by the conventional two electrode method. Ion conductances deduced in the above two papers^{11,14} differ markedly from those obtained (by Fowler's¹¹⁰ method in all three cases) from Kraus'⁸ data and from each other. Further discussion of this point will be postponed till Section IV.

Reasons for the difference in K_D values for the alkali perchlorates obtained in this work, and by Accascina and Schiavo,

are not immediately apparent, although slight disagreement in Λ values can obviously cause large variations in the slope of the Fuoss plots (see III. 5.2).

As mentioned above, results obtained by the potentiometric method in this work show all the five salts investigated to be dissociated to a certain extent in acetone. However, all show ion pair association and determination of Λ_0 from an extrapolated Onsager plot (Λ against $C^{\frac{1}{2}}$) is not permissible. (see below). The extent of the ion association can be indicated approximately by the deviation from the Onsager equation (III.5) :

$$\Lambda = \Lambda_0 - S C^{\frac{1}{2}}$$

The theoretical slope $|S|$ of the Onsager equation is less than that found experimentally

$$\text{i.e. } |S|_{\text{theoretical}} < |S|_{\text{observed}}$$

This can be shown, for example, for ammonium perchlorate which has the highest dissociation constant, K_D , measured. The Onsager plot is shown in figure 16 with the Onsager slope. The theoretical slope is $-742.25 \text{ cm}^{\frac{1}{2}} \text{ ohm}^{-1} \text{ mole}^{-\frac{3}{2}}$ as calculated from $S = \alpha' \Lambda_0 + \beta$ (table 5. 21) and the experimental value is $-1,195.2 \text{ cm}^{\frac{1}{2}} \text{ ohm}^{-1} \text{ mole}^{-\frac{3}{2}}$, which differ by a factor of 1.6. The deviations will be even larger for the more associated electrolytes. Further indication of the inadequacy of an Onsager plot is given by the data plotted in this manner for sodium perchlorate in figure 17. A distinct sigmoid shape is observable. This sigmoid shape has been noted by several authors,

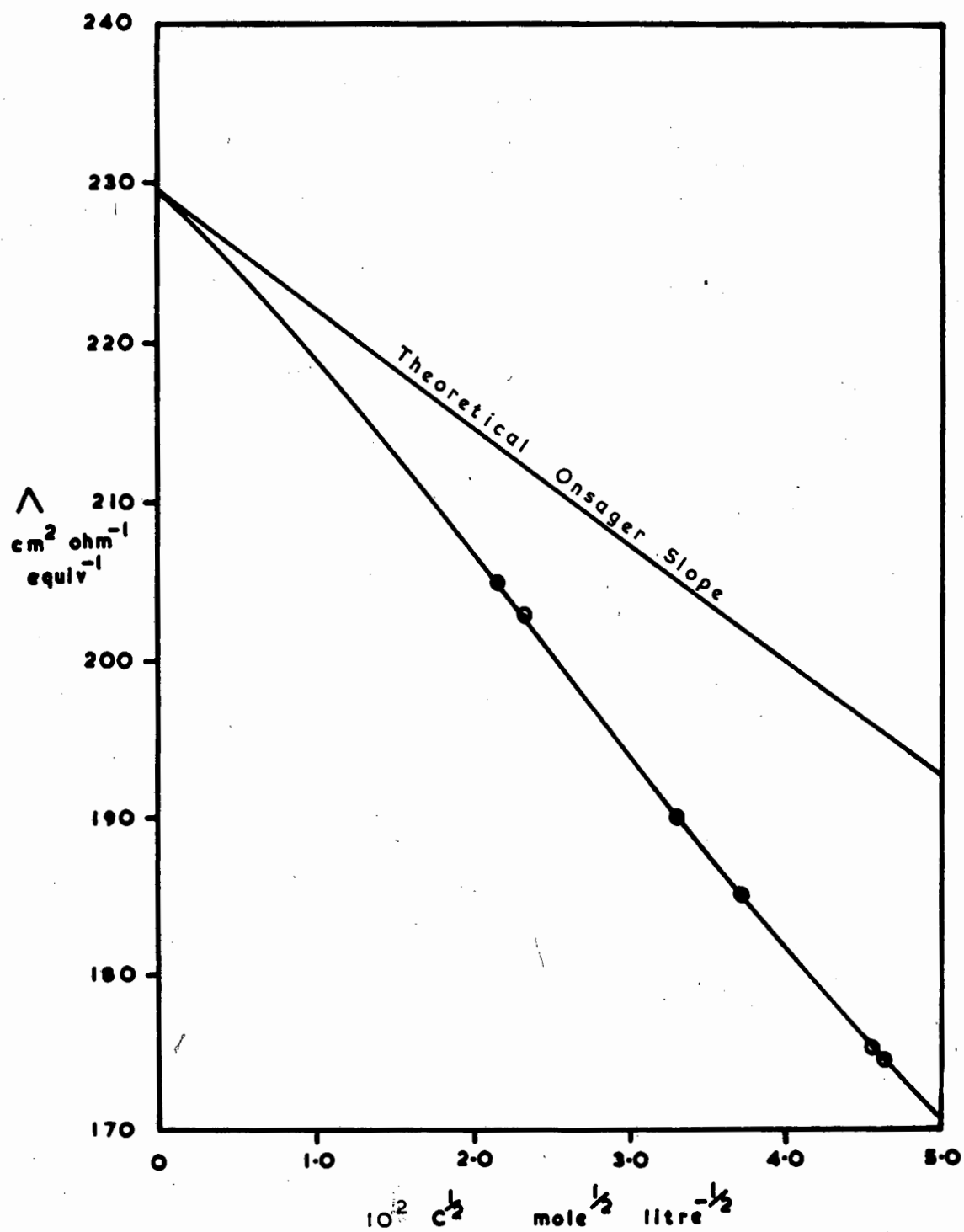


Fig.16. Onsager Plot for Ammonium Perchlorate.

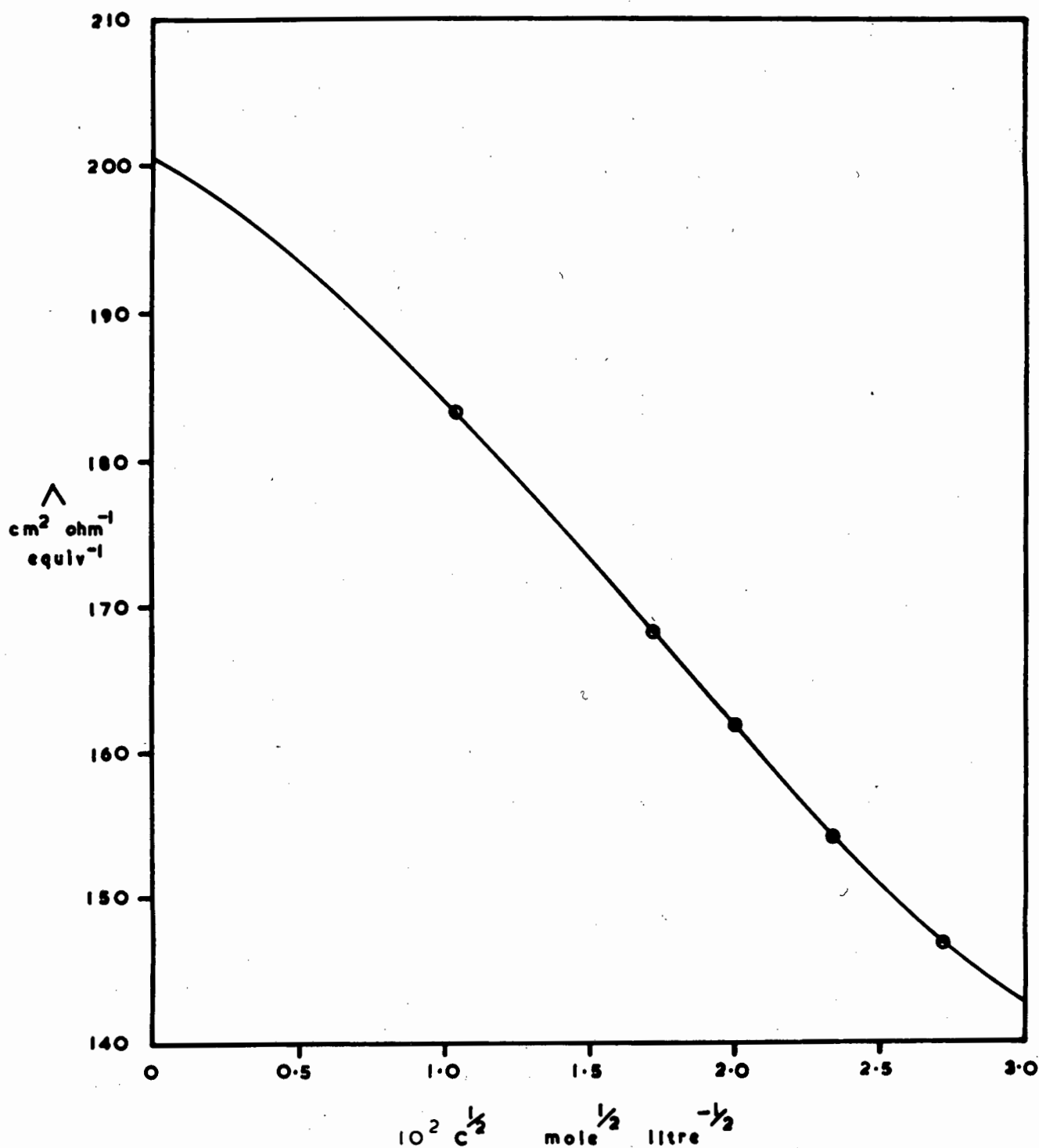


Fig. 17. Onsager Plot for Sodium Perchlorate.

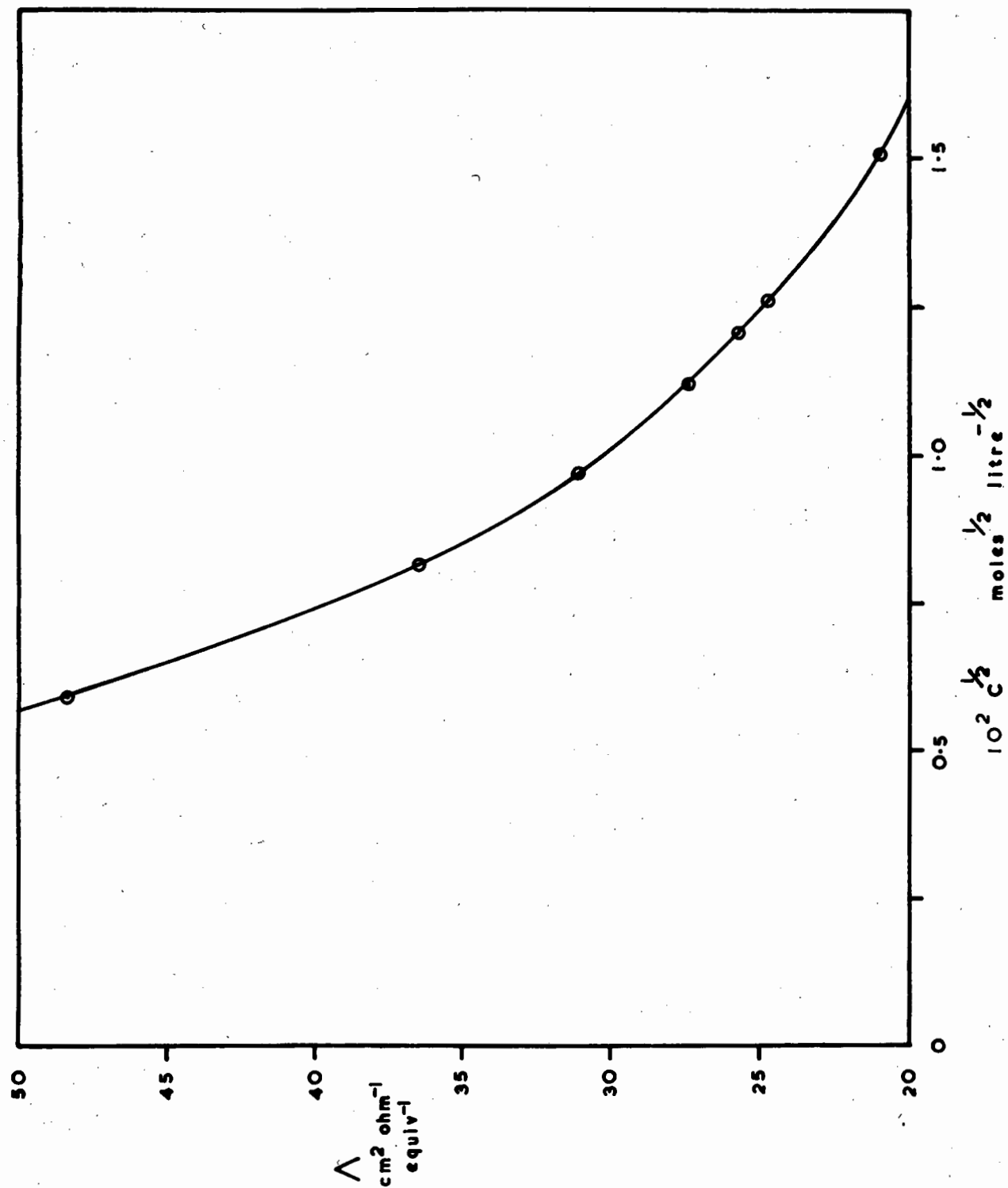


Fig.18. Onsager Plot for Lithium Chloride.

including Gordon⁷² and co-workers. A Λ vs. $c^{\frac{1}{2}}$ plot for LiCl, which has a low dissociation constant of 2.9×10^{-6} is shown in figure 18. Extrapolation is obviously almost impossible, and clearly conclusions as to Λ_0 and K_D data from any Onsager plots are not only inaccurate, but also invalid.

Acetone has a relatively low dielectric constant (20.47) and viscosity (0.00304 poise). It is a non-hydroxylic solvent and hence anions may be expected to be non-solvated.^{9,11} In general it might also be expected that large ions would have lower conductances than small ones. It seems to be fairly well established⁶⁷ in a variety of solvents that the size of the alkali metal ions in solution decreases from lithium to caesium.

A series of salts with the same anion and different cations might be expected to show a decreasing Λ_0 with increasing solvated cation radius, assuming the anion in acetone to be non-solvated. Table 13 shows that the results of this work for the alkali perchlorates do not follow these expectations. Potassium perchlorate can be considered anomalous in its equivalent conductance.

TABLE 13 ...

TABLE 13.

SOME CONDUCTANCE DATA IN ACETONE.

Salt	Λ_o	$10^4 K_D$	Reference
Li Pic	158.1	10.3	Kraus ⁸
Na Pic	163.7	13.5	Kraus ⁸
K Pic	165.9	34.3	Kraus ⁸
NH ₄ Pic	180.2	11.1	Kraus ⁸
LiClO ₄	195.4	6.3	This Work
NaClO ₄	200.4	16.5	This Work
KClO ₄	189.1	32.7	This Work
NH ₄ ClO ₄	229.5	72.4	This Work
LiI	194.8	96.9	Savedoff ¹⁴
KI	197.4	84.1	Savedoff
KI	192.8	80.2	Kraus
KI	196.6	91.3	Dippy and Hughes ³

Kraus⁸ gives conductances of the alkali picrates with the Λ_o trend given in table 13. This shows that for this anion Λ_o does increase from lithium to potassium. Also Savedoff's¹⁴ data (recalculated by the Fuoss method for comparison) for Λ_o of the Li and K iodides show a similar trend. It can be seen that the trend is not observed if Kraus'⁸ value of $\Lambda_o = 192.8$ for KI is used. However, Dippy and Hughes,³ very carefully determined Λ_o value for KI does agree with that of Savedoff somewhat more closely than Kraus. Savedoff does not regard the difference between her result and that of Dippy and Hughes as significant, although it is far greater than the relevant combined experimental errors.

Thus, ignoring Kraus' Λ_0 value for KI, the trend of increasing Λ_0 from lithium to potassium holds for the picrates and iodides and for lithium and sodium perchlorate. Potassium perchlorate alone appears to be anomalous in that Λ_0 decreases from 200.4 $\text{cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ for sodium perchlorate to 189.1 for potassium perchlorate. Accascina (using the conventional method) also found potassium perchlorate to be anomalous, although his figures differ somewhat from those found here (Table 12). The anomalous position of KClO_4 with regard to its relatively extremely low solubility in acetone as compared to LiClO_4 and NaClO_4 has been mentioned previously (III.4.2).

The above argument rests on the assumption that the solvated cation radius decreases from lithium to potassium with the perchlorate anion remaining unsolvated. Since Λ_0 values for the perchlorates are inconsistent with this, the assumption may be incorrect and the anion may be slightly solvated to an extent depending on the cation. It seems clear that the effect of cation-anion interaction and even ion-dipole interaction should also be considered in acetone as well as ion-solvent interaction. The reason for this is clear when it is realised that the interaction between ions depends on charge, size and polarizability and even dipole moment. It also depends on interaction of the ions with the solvent which in turn depends on structure, size, polarizability and dipole moment of solvent molecules. These two interactions are interdependent, as the latter increases the former decreases. Also

ions as they exist in ion pairs are not necessarily identical with free ions in solution. The solvent molecules attached to solvated ions may be squeezed out on pairing.

Consideration of the variation of K_D with cation size shows that K_D increases from lithium to potassium for the picrates (Kraus⁸) and perchlorates (this work) as shown in table 13. Since the energy necessary to separate an ion pair is a function of the ion-ion distance, then ion pairs with large ions should have relatively large dissociation constants and vice versa. This suggests the (solvated) cationic radii might increase in the order $\text{Li} < \text{Na} < \text{K}$, just the converse of the variation indicated from Λ_o values. Kraus,⁷¹ however, believes that the ions in the ion pairs of his alkali picrates⁸ do not differ greatly from the free ions. However, Savedoff's K_D for LiI is greater than any K_D for KI , suggesting that the solvated ionic radius of Li^+ is greater than that of K^+ .

Thus it is apparent that solvent effects are not the "key" to the problem as suggested by Hughes and Hartley,⁹ who, of course, had limited and less accurate data to consider. It is clear from the foregoing discussion of K_D and Λ_o values that the free ions in the solution and ions in the pairs are not necessarily of the same size. Consider the $10^4 \times K_D$ values for NH_4ClO_4 (72) and NH_4Pic (11) compared to LiClO_4 (6) and LiPic (10). NH_4ClO_4 has a much higher dissociation constant than NH_4Pic suggesting that the perchlorate ion in an ion pair is larger than the picrate

ion in an ion pair. However LiPic has a larger dissociation constant than Li ClO_4 . This indicates that specific cation anion interaction also plays an important role. Thus not only are free ions in solution and ions in the pairs not the same size, i.e. probably different entities as regards solvation, but the same cation probably interacts specifically with different anions and correspondingly for an anion interacting with different cations.

Kraus⁸ suggests that steric effects must have a marked influence on the dissociation constant, which is one aspect of specific ion-ion interaction. Another factor to be considered is that although ion pairs are electrically neutral, they still possess a dipole moment resulting in ion-dipole interaction as well.

Acetone is a dipolar aprotic solvent (dipole moment 2.72 D) and, by definition,⁶¹ cannot form strong hydrogen bonds as it cannot donate suitably labile hydrogen atoms. Parker,⁶¹ contrary to suggesting that anions might be non-solvated,^{9,11} states that anions are solvated by ion-dipole interactions with a superimposed interaction due to mutual polarisability of the anion and solvent molecule, which is greatest for large anions. However, he agrees that anions in non-hydroxylic solvents will tend to be poorly solvated. Thus we might expect that the order of anion solvation may be that of size i.e. picrate > perchlorate > iodide > chloride. However, no correlation of this with the data of tables 12 and 13 is apparent, and we may conclude that anion solvation in acetone is not a dominant factor; and is probably less than cation solvation. Kraus⁷¹

has stated that the size of halide anions in acetone appears to decrease from Cl^- to Br^- and that the charge distribution on the picrate ion results in a reduced picrate ion-acetone molecule interaction.

The very low dissociation constant of 2.9×10^{-6} for LiCl is noteworthy. Parker⁶² concludes that lithium salts dissolve largely as ion pairs in acetone, which is certainly the case for lithium chloride. Savedoff's¹⁴ K_D agrees satisfactorily with that of this work considering the very low value of this dissociation constant. The Λ_o value of 214 ± 4 obtained by the above author is higher than the 202.1 ± 0.2 of this work, but as the limiting ionic conductances for Li^+ found in the above paper vary from 78 to 93 $\text{cm}^2 \text{ ohm}^{-1} \text{ eq.}^{-1}$, as found from the equivalent conductances of lithium halides, with 93 from $\Lambda_o = 214$ for LiCl , possibly Savedoff's value is too high. (See IV. 7)

Lithium salts form solvates with acetone,⁶¹ and from an infra-red study of LiClO_4 in acetone, Pullin and Pollock⁶³ conclude that complexes of the type $\text{Li}^+ - (\text{acetone})_x$ are present in such solutions, with $x = 2$ in more concentrated solutions (ca. 0.3 mole fraction) and x possibly greater than 2 in the more dilute solutions. With a few measurements on NaClO_4 solutions they found a similar but less marked effect. These complexes may explain in part the high solubility of LiClO_4 in acetone, and the somewhat lower solubility of NaClO_4 . The solubilities in acetone at 25° of the salts used in this work are shown below:

	LiClO_4	NaClO_4	KClO_4	NH_4ClO_4	LiCl^{69}
Solubility g/100 ml solution ¹²²	76.4	36.6	< 0.155	1.77	3.94
(Molarity) _{max}	7.18	2.99	< 0.011	0.15	0.927

The low solubility of KClO_4 and its anomalous conductance may be due to the lack of such complexes, but independent investigations of this have not been made. Investigations for the other four salts listed above (other than LiClO_4) by such infra-red techniques may throw further light on this problem.

Thus it can be stated that in general the dissociation constants found reflect anion-solvation effects, that cation solvation is probably greater than anion solvation, and the low dissociation constant of LiCl is in accordance with the general tendency of such chlorides to be weak electrolytes in differentiating solvents (see below) such as acetone. Possibly the ions in the ion pair of LiCl in solution do not differ greatly from the unsolvated ions, which also would result in a low dissociation constant since the unsolvated Li^+ ion is small. (this will be discussed further in part IV).

The conductance of perchloric acid and its relation to other conductances is extremely interesting. As far as is known it is the only relatively strong acid in acetone, and is one of the strongest in water. The conductance of HCl in acetone at 25° was measured by Hotz¹⁶ and Sadie¹³ who found it to be very weak, as did Ross Kane⁹ with $K_D \sim 10^{-7}$. Plots of Λ against $c^{\frac{1}{2}}$ could not be

extrapolated for HCl as might be expected for such a low dissociation constant, but a Fuoss plot which was not a straight line, due possibly to HCl - acetone or $(\text{HCl})_x$ complexes,¹⁶ gave an approximate value¹³ of $\Lambda_o = 444 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq.}^{-1}$. Hence it might be expected that perchloric acid would have a very high conductance, since the limiting ionic conductance of the chloride ion is about $100 - 120 \text{ cm}^2 \text{ ohm}^{-1}$. However, this work obtained the value for HClO_4 of $\Lambda_o = 214.0 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$, with $K_D = 6.7 \times 10^{-4}$. (table 6. 2.1). No other determination of the conductance of pure anhydrous perchloric acid in pure anhydrous acetone has been traced in the literature. As mentioned previously, the potentiometric method ensured that no additional catalysis of solvent deterioration by platinum black, in the presence of perchloric acid, could occur.

Perchloric and hydrochloric acids are both strong acids in water. In acetone they have markedly differing dissociation constants of 6.7×10^{-4} and about 5×10^{-7} respectively. A possible partial explanation for the relative weakness of HCl will be given below. Once again specific cation-anion and ion-solvent interactions may both be important. Janz and Danyluk²⁹ have mentioned that differentiating solvents, such as acetone, give very different strengths to a series of electrolytes (e.g. alkali halides) as opposed to levelling solvents such as methanol, where a series will have similar strengths. Acetone has this differentiating property since it is a dipolar aprotic solvent and therefore should not efficiently solvate small anions, but should be slightly more

efficient for large ones.⁶¹

Perchloric acid is very much stronger than hydrochloric acid in acetone which means the bond between hydrogen and perchlorate ions is weaker than between the hydrogen and chloride ions. The solvation state of the entities concerned in the two 'ion-pairs' in acetone is unknown. However, if the perchlorate anion is larger, and hence more polarisable than the chloride anion, and not fully solvated in the ion pair, it can be more efficiently solvated⁶¹ than the chloride ion and thus will assist dissociation of perchloric acid in acetone relative to hydrochloric acid. Thus solvation of the anion will reinforce the 'absolute' acid strength of perchloric acid, which is the tendency for the acid to dissociate in the absence of other molecules.

It would be instructive to measure accurately the dissociation constants of the other halogen acids and picric acid in acetone. Other factors may play a larger or smaller part such as formation of molecular HA complexes.^{29,16,27} Dihalide ions, HX_2^- , are a fairly common species.

Braude,³⁰ using acidity functions, found the proton to be moderately solvated in acetone and showed the existence of the Me_2COH^+ complex. It is probable that most, if not all, factors mentioned are important to some extent. Further discussion of ion pair and single ion sizes will be postponed to Section IV.

The effect of possible residual moisture present in the

solutions will be examined briefly. The moisture content of the acetone was generally about 0.003% (II). The change in conductivity for several electrolyte solutions in acetone has been found to be directly proportional to the amount of water present for small amounts of water.⁹ This direct proportionality has also been found in alcohols,⁹ methanol⁷⁰ and dimethylformamide.¹⁷ The greatest fall in equivalent conductance recorded for 1% addition of water⁹ to 'dry' acetone solutions is about 10%, and more often values of about 5% are recorded. (As mentioned previously, Ross Kane's⁹ data are suspect, but these figures will suffice for this argument.) Hence, unless the first trace of water ($< 0.003\%$) has an unusually and unexpectedly large effect, the results obtained here cannot differ from those in completely anhydrous acetone by more than 0.03%, which is within the experimental error and the difference may well be smaller. In addition of course, a solvent correction was always applied. Dippy and Hughes,³ using acetone with 0.18% moisture, find a solvent correction to be a satisfactory procedure provided it is low and constant, as was the case in this work. However, Kraus⁸ prefers the criterion that the solvent correction should be negligible.

It is apparent that attempts to correlate limiting equivalent conductances quantitatively with other physical properties are necessarily limited. Limiting ion conductances are essential in order to give further insight into phenomena in electrolyte solutions.

Gordon and co-workers²⁴ stated in 1953 that unless ion conductances become available further such correlations are "doomed to failure."

The following section deals with transference in acetone.

PART IV.

TRANSPORT NUMBERS AND IONIC CONDUCTANCES IN ACETONE.

IV.1 Introduction.

As indicated in the previous part a vast amount of literature exists dealing with equivalent conductances in anhydrous solvents. Conductances have been measured, for example, in alcohols,^{46,24} hydrogen cyanide,⁹⁷ amides,^{17,80,98} benzene,⁷⁷ and derivatives of benzene, pyridine,⁷⁸ dimethylsulphoxide,¹¹⁴ dioxane,⁷⁵ and substituted paraffins⁷⁹ and olefins,⁷⁶ besides acetone. In 1959 Robinson and Stokes⁹⁵ stated that 'the theoretical interpretation of the (conductivity) results is at present hampered by a severe shortage of reliable transport numbers in anhydrous solvents.' The need for accurate transport numbers becomes even greater with each conductance measurement. Attainment of a better understanding of phenomena such as ion-solvent and interionic interactions in electrolyte solutions, requires information about ionic sizes and solvation properties as well as ionic conductances themselves. Prior to 1959, transport data had been obtained in ethanol^{83,87} and methanol^{83,89} and subsequently, excluding this work, precise measurements have been made in only four anhydrous solvents, namely, dimethylformamide,¹⁷ nitromethane⁹¹ and formamide⁸⁰ at 25° and liquid ammonia at much lower temperatures.⁸² The latter solvent is one of the rare cases where transference measurements are available

but no accurate conductance measurements.⁸² This represents the sum total of all accurate transport numbers in solvents other than water. All the accurate work mentioned above was obtained by the moving-boundary method, which can give results more accurate and precise than the e.m.f. or Hittorf methods in such cases.^{10,80,107,108} In addition the moving-boundary method is far more rapid¹⁰⁷ than other methods and several results can be obtained from one experiment.

In this section precise transference measurements in acetone will be presented. Earlier attempts to measure transport numbers in acetone were made by Erdey-Gruz²⁵ and Sadie¹³ by the e.m.f. method. They were unsuccessful in that accurate transport numbers at infinite dilution could not be deduced because measurements were limited to a few approximate ones at high concentrations. Sadie¹³ concluded that some other more refined method should be used.

IV. 2 Choice of Method.

The literature surveyed above shows that for precise work in anhydrous, non-aqueous solvents at low concentrations there is, in reality, no choice of fundamental method. The moving-boundary method¹⁰⁷ is the only one offering any apparent hope of success with a reasonable degree of accuracy.

It is evident that some, if not all, of the reasons for the lack of progress in determining transport numbers in non-aqueous solvents are due to experimental difficulties. In most solvents of low dielectric constant ion pair formation occurs which means that

transference measurements, to be correctly interpreted,²⁶ should be carried out at low concentrations ($< \text{ca. } 0.01\text{M}$). However, the normal optical methods for following a moving boundary⁸⁵ become unsuitable at very low concentrations, because of extremely small differences in refractive indices between leading and indicator solutions.

Lorimer, Graham and Gordon²⁶ have developed a conductimetric method for following the boundary which has been applied to solutions of alkali halides in ethanol⁸⁷ and quaternary ammonium halides in nitromethane.⁹¹ Essentially this method involves following the passage of the boundary along a moving-boundary tube by detection of the resistance change which occurs as the leading solution is replaced by the indicator solution. The experimental difficulties associated with this method have also been found to be very great, (IV. 6). However, results can be obtained at low concentrations without any requirements as to the optical properties of the indicator solution, the choice of which is hence less restricted.

In non-aqueous solvents at low concentrations of weak electrolytes the resistance through the transference cell from anode to cathode becomes very high, and hence disturbance of the boundary due to Joule heating⁸⁸ will occur. It is thus necessary to use low currents (less than $\text{ca. } 0.1 \text{ mA}$), but with the optical procedure of following boundary movement there is always a minimum current below which the boundary becomes too diffuse for precise observations. The conductimetric method does not have this restriction, and is

suitable for concentrations well below those of other procedures.

Hence it was decided to adopt this approach in this work.

IV. 3 Apparatus.

A brief description of the conductimetric method will be given followed by detailed descriptions of the apparatus.

The conductimetric moving-boundary method as used in this work involved passing a small, constant, direct current of known magnitude through the leading and indicator solutions contained in a calibrated moving-boundary tube or channel. The passage of the boundary along the tube was followed by measuring the increase in resistance across the tube, ΔR_c , by means of microelectrodes sealed into the walls of the channel at intervals along its length. ΔR_c was detected, amplified and converted into a voltage change by means of a detection device. The voltage change was monitored on a recording millivoltmeter, and by this means the time of boundary passage could be recorded. The constant current was supplied by an electronic device and measured potentiometrically.

3. 1. The Constant Current Device and Current Measurement.

A small constant current of accurately known magnitude was required. The device was based on that described by Hopkins and Covington⁹⁰ for supplying current constant to within 0.2%. The current, for the acetone solutions in particular, was necessarily small to prevent resistance heating in the channel from causing boundary instability or displacement of the boundary leading to inaccurate results.

For this investigation the constant current source was required to supply a maximum of about 1 mA over a three fold load impedance change in the approximate range 0.2 - 4 Mohm. The device of Hopkins and Covington was constructed from valves which are unobtainable and for which no equivalents could be found, and could not deliver a constant current below 0.5 mA.

Figure 19 shows the modified device with the valve types used in this work, which enabled a minimum constant current of 0.3 mA to be obtained, which was quite satisfactory for cell calibrations. However, in acetone lower currents were required to prevent excessive Joule heating and resistors R_4 and R_{10} were changed from 10 k ohm and 3.3 k ohm respectively, to 3.3 k ohm and 4.7 k ohm, which enabled a constant current of between 0.08 mA and at least 1.0 mA to be obtained.

The current supplied could be varied with the current control potentiometer RV_2 (figure 19.). RV_1 is the stabilisation control and a position could be found on this potentiometer for which a change in load impedance by a factor of five produced less than 0.2% change in current. The device was warmed up before use for at least an hour on a dummy load, D, and connection between the device and the moving-boundary cell, C, was made by a d.p.d.t. ceramic 'make-before-break' switch, W.

Current was measured to $0.01\mu A$ by measurement of the potential drop across a standard 1,000 ohm Muirhead Type A60 resistor

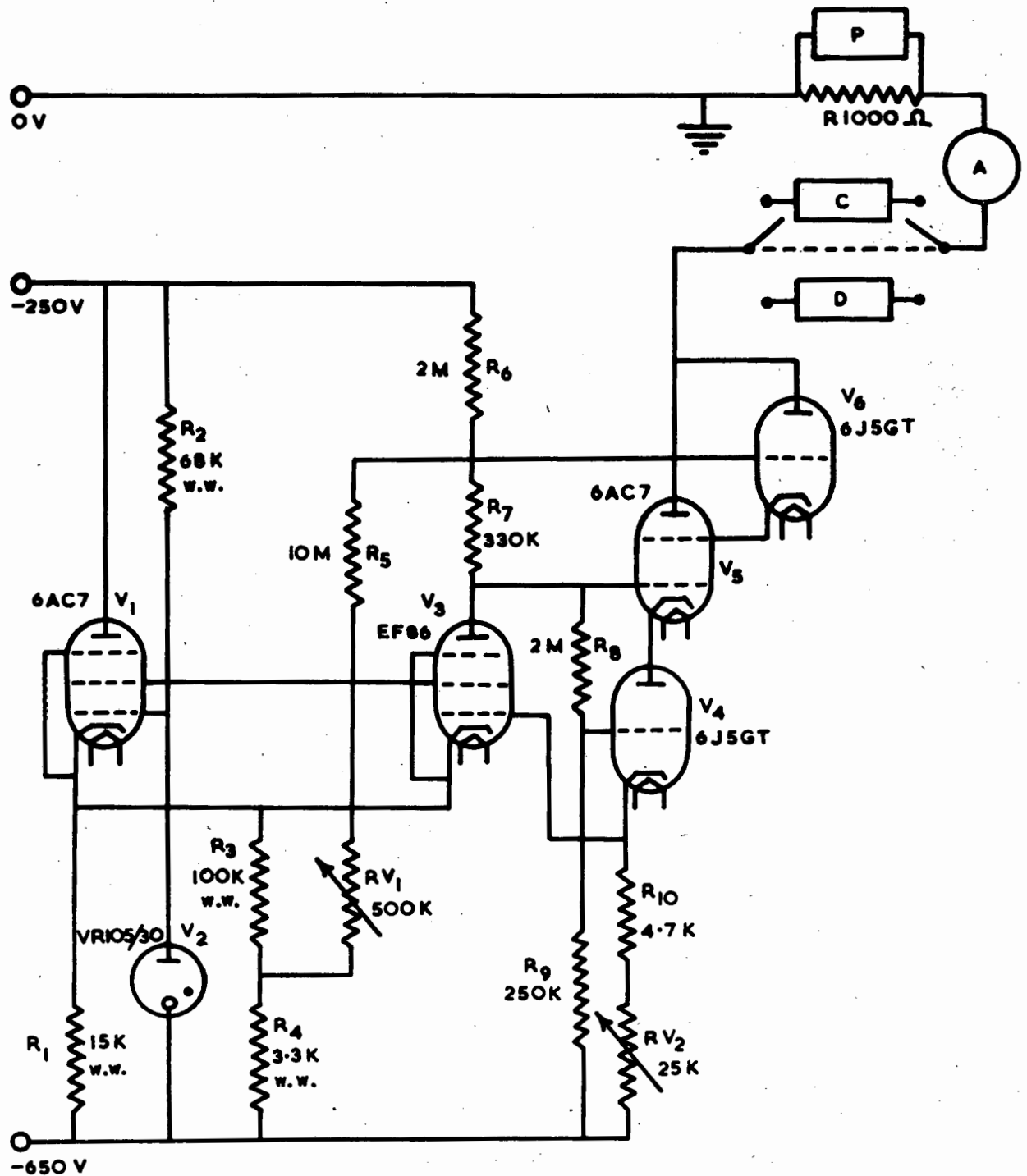


Fig. 19. Constant current device circuit diagram

in series with the cell. The standard resistor had been certified at 20° , 25° and 35° with a precision of 0.005% by the N.P.L., England. A PYE Type 11330 galvanometer preamplifier was used in conjunction with a Scalamp galvanometer type 7901/T and a Tinsley type 4025C potentiometer, which resulted in an overall sensitivity of approximately $40 \text{ mm}/\mu\text{V}$. The standard Weston cell used was a Tinsley Type 1268.

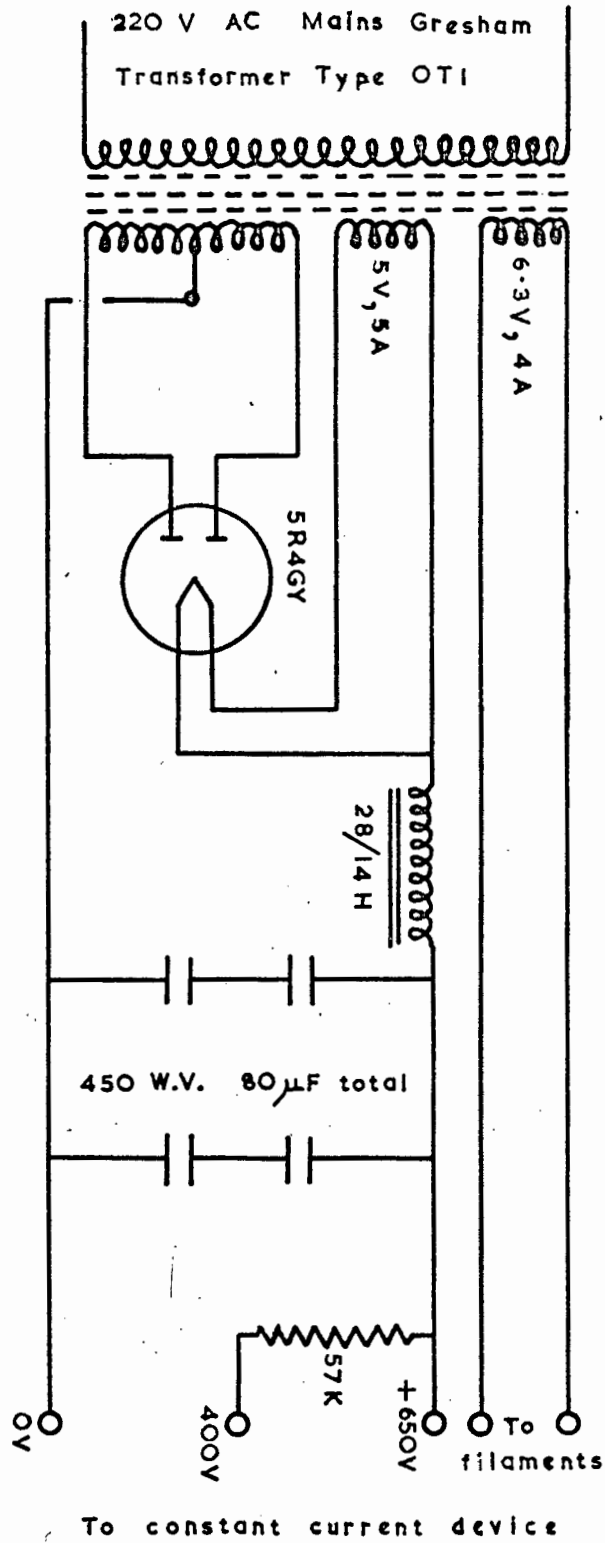
It will be observed (figure 19) that an unusual feature of this constant current device is the earthed positive lead. This was used in order that the potentiometer circuit may be near earth potential to reduce the risk of electrical leakage within it.⁹⁰

The power pack circuit for the constant current device is shown in figure 20. The $80 \mu\text{F}$ bank of condensers shown in the figure was used to step up the output voltage as a transformer giving 650 V was not available. In order to prevent possible insulation breakdown the porcelain valve holder for the full-wave rectifying valve V_I was mounted on a Perspex sheet fastened along its edges to the aluminium chassis some three inches from the valve holder. The positive 650 V lead (figure 20) was earthed as required for the earthed positive operation of the device.

3.2 The A.C. Detection Device.

The transistor in the transistorized detector mentioned in the paper of Gordon and co-workers²⁶ had a tendency to burn out.⁹² Hence a new detector was designed using suggestions of Dr. J.L.N. Besseling, of the Electrical Engineering Department of the University of Cape Town.

Fig. 20. Constant current device power pack.



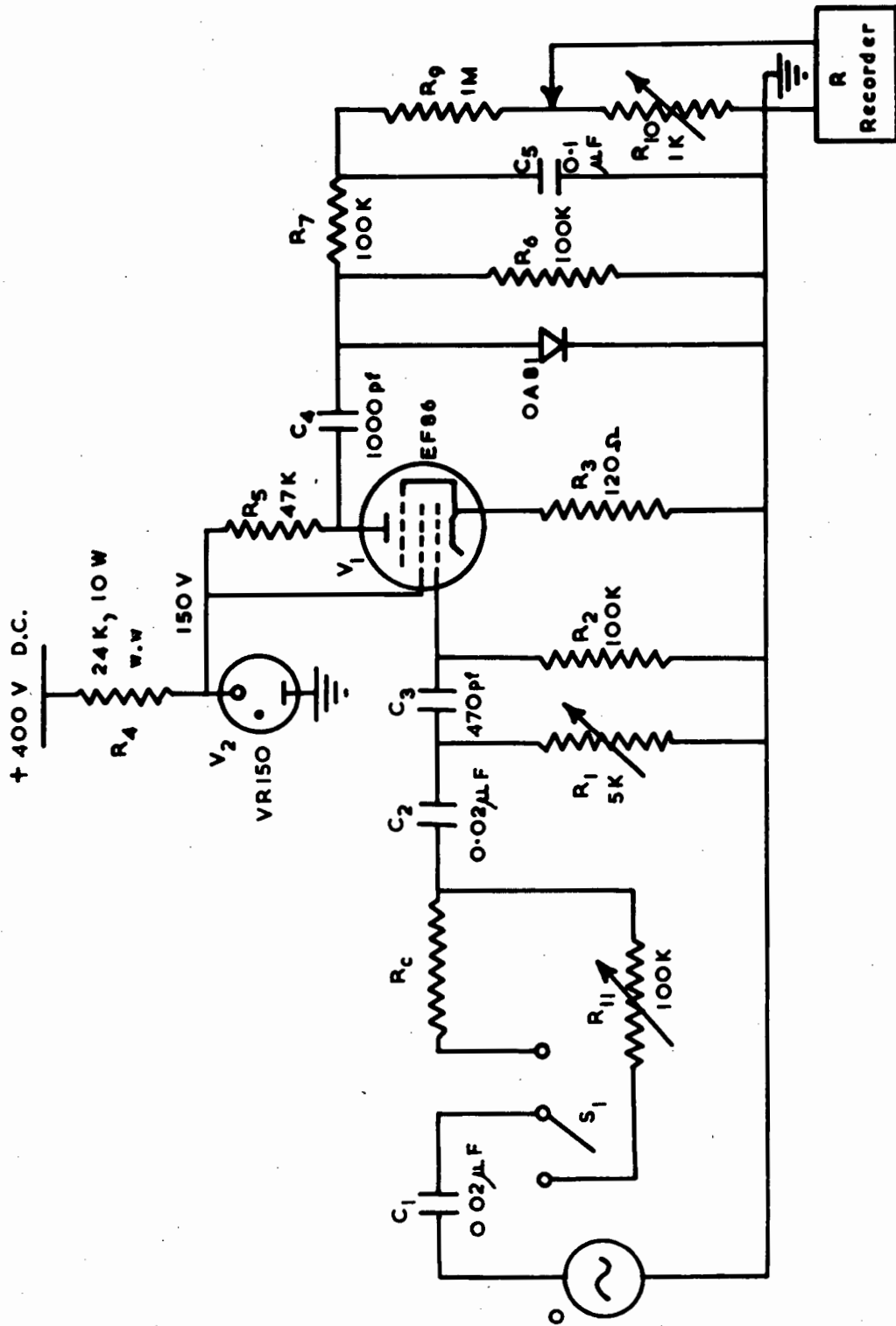


Fig. 21. A.C. Detection Device.

A signal from the oscillator O (fig. 21) was passed through the cell whose resistance is R_c and the signal change due to variations in R_c as the boundary passed along the tube were amplified, rectified and monitored as a voltage change on the recording millivoltmeter, R.

The requirements for the approximately 20 kc/s oscillator were that it should have a variable power output (0-6V) and have less than 1 k ohm output impedance. A Hewlett Packard Model 200 - CD wide range oscillator with Z_{output} of 600 ohms was used in the initial trial experiments and subsequently a Hewlett Packard Model 205 AG audio signal generator was used. It is important that the circuit be made sensitive to changes in R_c , the resistance across the channel between a pair of microelectrodes. For optimum response to changes in R_c a small oscillator output impedance is necessary. The power output was variable, so that, for a given R_c , and other control settings, the oscillator power could be adjusted until a suitable deflection was obtained on the Texas recorder, R. The power was kept at a minimum to keep resistance heating in the boundary tube as low as possible.

The detection microelectrodes, sealed into the walls of the boundary tube, were capacity coupled via C_1 and C_2 as shown (fig. 21) to enable continuous recording by blocking the direct current flowing in the cell which would be offered an alternative path if the blocking condensers C_1 and C_2 were not used. These condensers were closely matched for phase and capacity and were 5,000 WV D.C.

capacitors with a leakage resistance greater than 100 megohms. The capacitors were enclosed in copper sheet shielding fastened to the earthed aluminium chassis. A 100K dummy linear potentiometer, R_{11} , could be switched in via the d.p.d.t. make-before-break switch S_1 . A switch of this type prevents violent oscillations of the recorder when the switch was operated. The dummy enabled the oscillator and amplifier to operate without passing current through the cell.

A shunt, R_1 , which is in effect a sensitivity control, was inserted as shown. This control, which for best response to changes in R_c must not be too large, was used to set the recorder at almost full scale deflection when the leading solution was between the microelectrodes.

Inspection of the circuit shows that the signal received by R is an inverse function of R_c and hence the recorder signal will decrease as the boundary passes. The sensitivity or gain control was thus used at the least value possible consistent with a near full scale recorder deflection. The A.C. signal was amplified by the EF 86 amplifier, V_1 , and then rectified by the OA 81 rectifier. External voltage changes did not affect the amplification since the HT voltage for V_1 , which was obtained from a 400 V D.C. power supply, was kept constant at 150 V by the voltage regulator, V_2 . To prevent damage to the recorder by sudden large signal changes, the voltage divider R_9, R_{10} was incorporated as shown. A recording milliammeter was unavailable and the signal was recorded using the

voltage change across the scale control, R_{10} , monitored on a Texas Instruments Model FWS recording millivoltmeter, R , which had a 1 mV full scale deflection. The scale control, R_{10} , was used in conjunction with the oscillator output control and the gain control, R_1 , when adjustment for optimum recorder response to changes in R_c was being made. All leads were shielded and the shields earthed.

The apparatus described above was found to be extremely sensitive to outside interference of any sort when properly adjusted for optimum response. When correctly adjusted with R_c ca. 12 k ohms, as was the case for calibrations with 0.001 N KCl, the oscillator output was only 1 volt for a 90% signal, i.e. 0.9 mV, on the recorder. This shows that resistance heating of the moving boundary solutions was in fact negligible. With R_c ca. 50 k ohms, as was the case for dilute acetone solutions, the oscillator output required was only about five volts.

3.3 Thermostats.

Uniform temperature control along the entire length of the boundary channel is of vital importance for achievement of accurate transference data. Non-uniform heating at any stage would result in a slight expansion (or contraction) of the solution with consequent displacement of the boundary.

The length of the tube was about 30 cm. and thermostating was achieved as described below. A large Perspex tank of internal dimensions $10\frac{1}{2}" \times 10\frac{1}{2}" \times 1'10"$ was about three-quarters filled with Shell Diala B Transformer oil. Oil was pumped at about

5 l/min. from the Buhler Superthermostat used in the conductance work (III. 2.3) into the tank at the bottom and removed near the top via short lengths of tygon tubing. The thermostat was set at a temperature slightly above 25° , depending on the ambient room temperature, a suitable constant temperature room being unavailable.

Cooling water, thermostatted at 22° with a Braun thermomix 11, was circulated through cooling coils in the Buhler thermostat. The thermostat was mounted on a mat of rubberised hair which effectively absorbed all vibrations, thus preventing disturbance of the boundary in the tank nearby. The transference cells were immersed in the oil except for about 1 cm from the open ends of the tubes (See IV 5.1).

The perspex tank was fitted with a wooden lid which had holes for a calibrated thermometer and stirrer. The thermometer was clamped and could be adjusted to enable temperatures to be read at various positions and depths in the tank. The stirrer was driven by a high speed electric motor and no temperature gradients were found in the tank. The stand holding the stirrer motor was mounted on a sponge mat which absorbed all vibrations, as was the Braun thermomix.

The thermostating arrangements described above enabled temperature to be controlled throughout the tank at $25.00 \pm 0.01^{\circ}$ as measured on the calibrated thermometer.

3.4 The Moving Boundary Cells.

Two cells were made, one for falling boundaries and one for rising boundaries. The design of the cells was based on the

fundamental one for a rising boundary cell used by Gordon and co-workers,⁹³ and sheared boundaries were formed using stopcocks as recommended by these authors and further discussed by Gordon and Kay more recently.⁹⁴

The procedure followed in constructing the transference cells was that suggested by Lorimer, Graham and Gordon²⁶ with certain major modifications.

3. 4.1 The Rising Boundary Cell.

A sketch of the cell is shown in figure 22 and a photograph showing construction details is given in figure 23.

The cell (fig. 22) is seen to consist of a four-way Gordon and Kay⁹⁴ type lll shearing stop-cock, made by Springham and Company Ltd., attached to a length of 2.5 mm. internal diameter tubing, the boundary tube, and to attendant filling tubes as shown. The stop-cock was marked in such a way as to enable the bore and boundary tube to be exactly and reproducibly aligned to enable precise shearing of the boundary and positioning of the stop-cock. The boundary tube holds five pairs of detection microelectrodes labelled 1 to 5 starting from the stop-cock. The detection electrodes were spaced about four cm. apart except for pairs 2 and 3 which were about eight cm. apart.

Compartments C and E were the electrode compartments, and were about 8.5 cm. long. These compartments were made as small as convenient to keep the total volume changes, due to slight temperature fluctuations, to a minimum. The cell was so designed

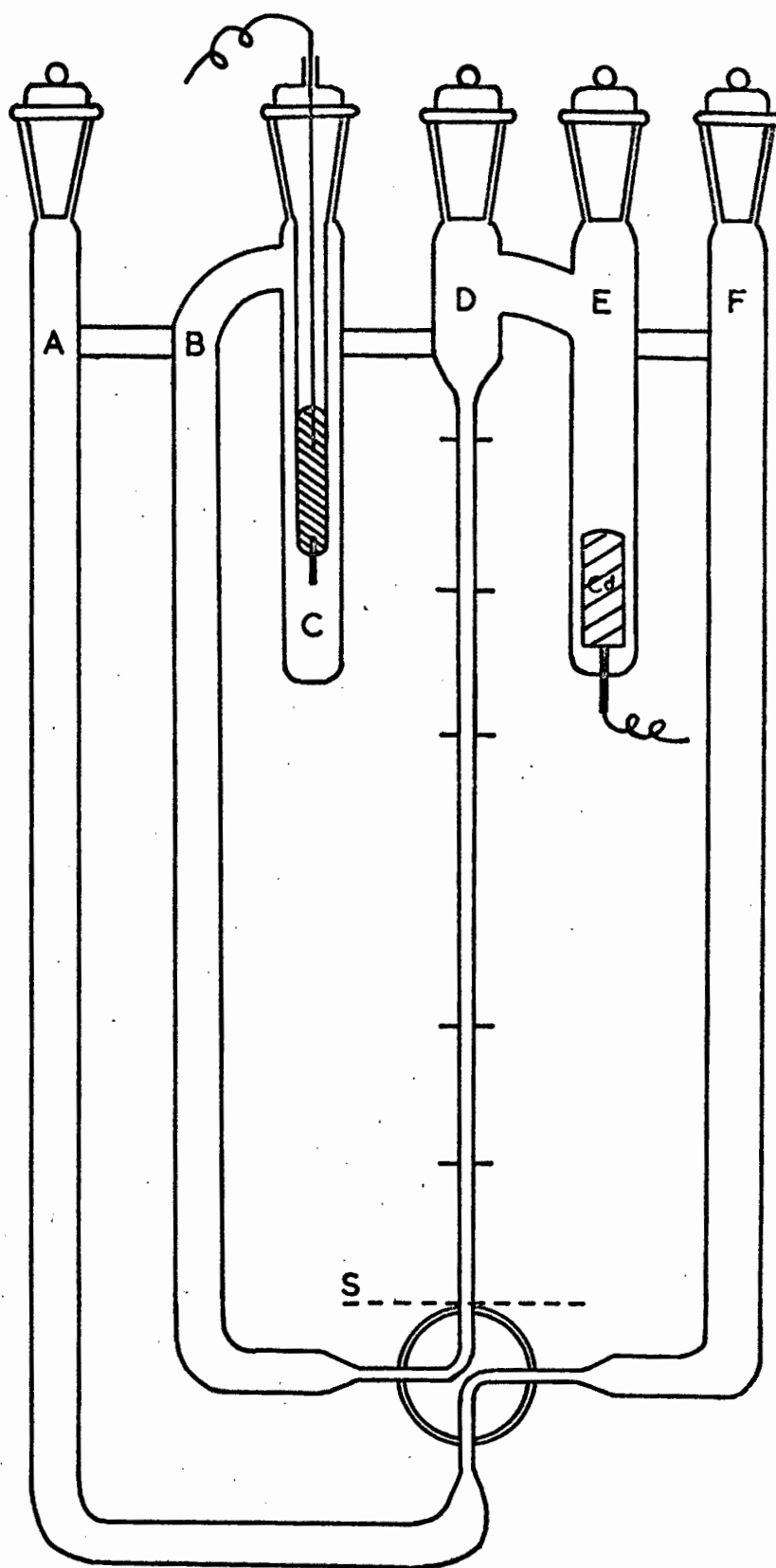


Fig. 22. Rising boundary cell.

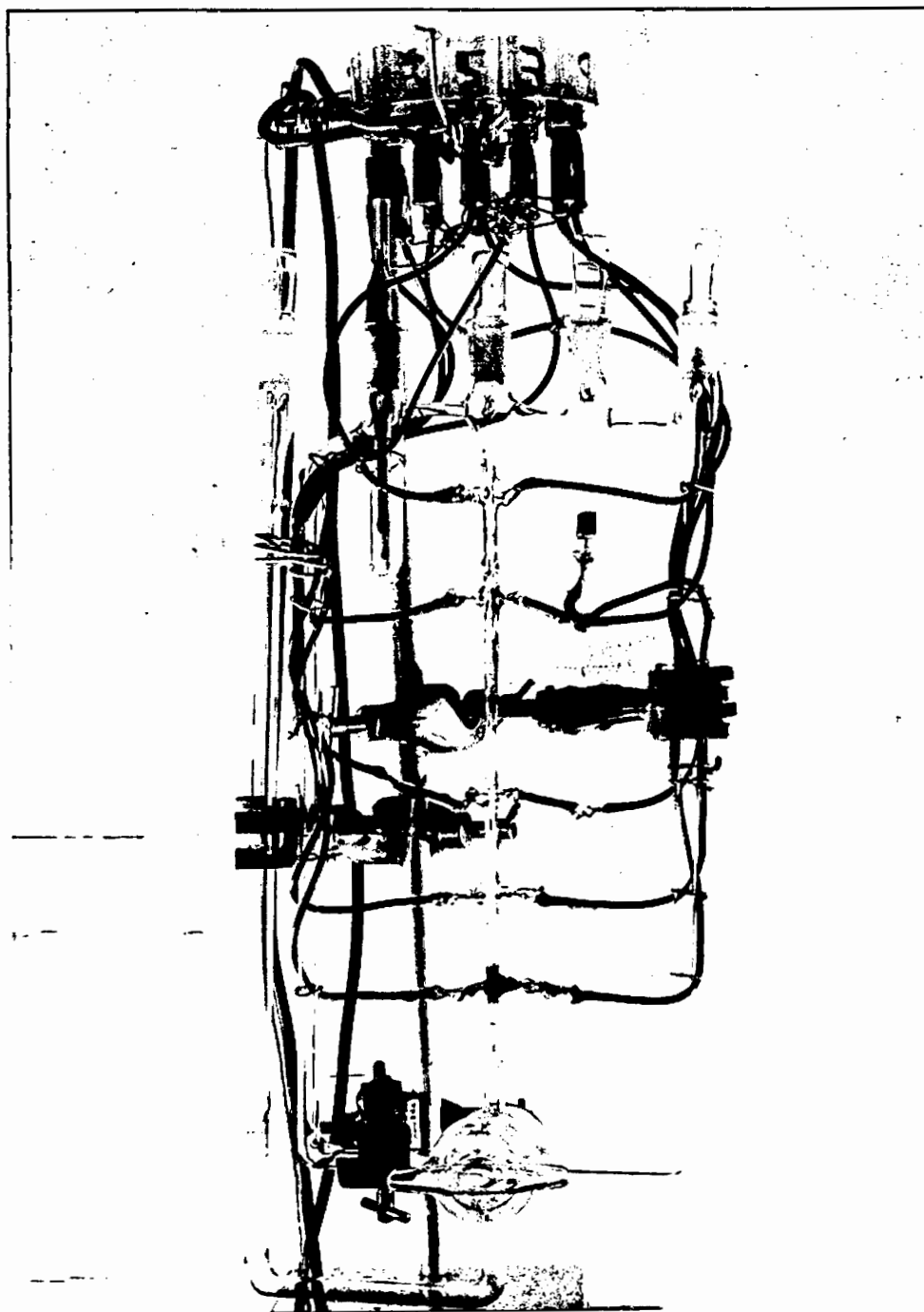


Fig. 23. Rising Boundary Cell.

that the solutions were not contaminated by the products of electrode reactions which remained in compartments C and E. All tubing other than the narrow bore tube mentioned above was of ca. 0.5 cm. internal diameter. The distance from the point of shear, in plane S, to the first electrode pair was about 4.8 cm., and from the fifth pair to the end of the narrow boundary tube was about 2 cm. In most cases compartment C held the cathode, which was a Ag/AgCl electrode mounted on a ground glass joint, and compartment E held the 1 cm. diameter, 1.25 cm. high cylinder of 99.99% pure cadmium anode, which was mounted on a stout platinum wire welded to an insulated copper lead from the constant current device. The anode had a 0.5 cm. deep, 1.4 mm. diameter hole drilled in it into which the platinum wire just fitted. The cathode consisted of a 2.5 cm. length of stout platinum wire, mounted in a glass tube joined to a male ground glass B14 joint, and thickly coated with AgCl by dipping into Riedel de Haen Analar AgCl fused in a platinum crucible. This AgCl layer was renewed at intervals when it showed signs of deterioration during the work. Electrical connection was made via a platinum wire, spot welded to the insulated copper lead to the constant current device, which dipped into mercury in the tube.

Operation of the cell will be described in IV. 5.1.

The method of constructing the boundary tube with its micro-electrodes and their connection to the A.C. detector will now be described.

As explained by Gordon and co-workers,²⁶ the electrodes must be as small as possible in the vertical direction, i.e. along the tube length, in order to improve the precision of measurement of time when the boundary passes the electrode pair, (this passage of boundary past an electrode pair will be called the 'event' from now on) and to minimise the possibility of them acting as bipolar electrodes to the D.C. current.

Platinum ribbon, 0.007 mm. thick and 1 mm. wide, was cleaned by soaking in a nitric acid-sulphuric acid mixture⁴³ and then thoroughly rinsed with distilled water and Analar carbon tetrachloride. It was dried at 100° and subsequently handled with nickel tipped tweezers. A 2.5 cm. length of the platinum ribbon was placed across an open end of a length of boundary tube, which was of ca. 2.48 mm. internal diameter and 0.7 mm. wall thickness. Another piece of tubing was fused to the former piece as recommended by Gordon and co-workers.²⁶ As shown in figure 22, five such joins were made. Several boundary tubes were prepared before one with five electrode pairs of similar 'cell factor' was obtained. The cell factor was obtained by measuring R_c across the tube when it was filled with 0.01 M KCl.²⁶

Great care was required when handling this partly constructed boundary tube, since the small pieces of platinum electrodes projecting from the walls of the tube were extremely fragile. The lengths of platinum across the inside of the tube were then cut off

using a thin straight steel rod sharpened at the end. Any remaining pieces of platinum were removed by rubbing them gently with a mixture of 3F fineness carborundum powder and glycerine using the steel rod.

The next stage was the joining of approximately 2.5 cm. lengths of 0.4 mm. diameter platinum wire to the ten fragile electrodes. This was achieved by mechanically joining the ends of the platinum using a pair of tweezers to bend the metal. A drop of solder on each join completed the seal. Although solder is not recommended for Pt - Pt seals, it was found that with a little care excellent joins were achieved. Attempts to have the metal spot-welded were unsuccessful in that a suitable instrument for this purpose, which did not burn away the fragile electrodes, was unavailable in Cape Town. The best instrument obtainable was as used by a manufacturing jeweller, which used such high temperatures over a rather large region that serious distortion of the boundary tube itself could not be avoided. Further investigation of welding procedures was abandoned, since soldering as described above resulted in excellent mechanical and electrical connections.

Gordon and co-workers²⁶ suggest supporting the platinum strips with a thread of glass fused to the wall of the tube. It was found in this work that this procedure was dangerous in that the fragile metal strips were too easily broken in the process, and the tube became distorted. This occurred whether the platinum wires were connected or not, and it was found impossible to support the leads

successfully in this manner.

Hence a new procedure was devised. The electrodes were covered with a suitable resin which could be hardened once in position. Shell epoxy resins, Araldite and other similar resins were found to soften or crumble when soaked in an acetone - carbon tetrachloride - methanol mixture for two or three days. These solvents were among those to be used for cleaning the outside of the cell and rinsing thermostat oil from it. A fibre glass material, Beetle polyester resin FB 90 made by British Industrial Plastics S.A. (Prop.) Ltd., was found to give a hardsetting resin when cured, which was insoluble in all solvents tried, and had excellent insulating properties.

The short platinum wires were covered with plastic insulation and soldered to shielded 3.5 mm. external diameter coaxial cable, the shields being earthed. All exposed portions of the wiring were covered with several layers of fibre glass resin, which also covered the boundary tube in the region surrounding the microelectrodes and the electrodes and leads themselves in such a way as to provide a solid insulating support. Insulation cable is not impervious to organic solvents, and hence all insulation likely to come into contact with oil or solvents was liberally coated with resin which was renewed periodically.

The upper ends of the electrode leads (fig. 23) were soldered to phone tip sockets and the screens connected to each other and thence to a phone tip socket. The sockets were plugged into holders

held in a Perspex ring of 4" external diameter, $2\frac{1}{2}$ " internal diameter and 1" thick. Two separate insulated 6 mm. diameter coaxial cables with earthed shields led from the Perspex ring to the A.C. detector. Any exposed wiring was covered with resin, and the resulting insulation leakage resistance was undetectable as measured on a Megger Type AP6496 megohm-meter, which registered infinity. A few days after constructing the apparatus, the leakage resistance had fallen to 4 M ohms. The reason was found to be surface conduction along the outer surface of the Perspex ring, due probably to a coating of dust, since cleaning of the Perspex raised the resistance to 'infinity.' Each socket holder was therefore surrounded by a quarter inch deep saw cut in the cleaned Perspex which effectively eliminated any leakage. The ring and attendant connections were covered with a plastic bag to prevent dust accumulating in the saw cuts.

The importance of having no other electrical path available for the D.C. boundary current other than through the solution is vital. A major part of the experimental difficulties involved with this work concerned elimination of possible leakage of the direct current. Gordon and co-workers,²⁶ who used a different system of leads exposed to the air, found current leakage to earth in humid weather a problem. Blum and Schiff⁹¹ overcame this problem using tubes filled with silica gel. Fortunately this difficulty did not arise in this work, possibly because the humidity was not high enough and possibly because a different wiring system using coaxial cable was used with coatings

of fibre-glass resin wherever possible.

After initial construction the cell was filled with a sulphuric acid - nitric acid cleaning mixture and soaked for 15 hours, followed by thorough rinsing with distilled and conductivity water, Analar methanol and carbon tetrachloride. After each experiment the cell was thoroughly cleaned and left overnight filled with an efficient cleaning agent, namely, 40% RBS 25. The thorough removal of every trace of grease from the moving boundary cell was found to be of the utmost importance for obtaining precise results. All stoppers had P.T.F.E. sleeves.

For calibration with aqueous solutions the shearing stop-cock was carefully greased with a minimum of Edwards high vacuum soft grease. For acetone solutions considerable difficulty was experienced in finding a suitable grease. Fischer Non-aq grease used in the earlier work (III) proved to be too dry and small flakes of grease, which appeared when the stop-cock was turned to shear a boundary, prevented formation of a stable boundary in acetone solutions. Every other grease tried dissolved to some extent in acetone. Hilflon aerosol P.T.F.E. dry film lubricant did not form a leak proof seal and silica aerogel greases were slightly soluble in acetone.

Over a period of a few hours, which was about the time for which the acetone solutions remained in the cell, it was found that Dow Corning silicone grease was not significantly dissolved. Hence a

mixture of silicone grease (30%) and Non-aq grease was used to grease the stop-cock in the region surrounding the bore. The 'outer' region was greased with Non-aq grease. Great care was taken to ensure that no grease whatsoever entered the apparatus. Immediately after completion of an experiment, the grease was completely removed and the stop-cock cleaned with carbon tetrachloride.

The cell was periodically filled with concentrated hydrochloric acid to remove surface alkalinity.

3. 4.2 The Falling Boundary Cell.

A sketch of this cell is shown in figure 24 and additional construction details in figure 25. It is seen to consist of a so-called Gordon and Kay⁹⁴ Type VIII shearing stop-cock at the top of the boundary tube with electrode compartments B and E as shown (fig. 24). The stop-cock was marked to enable the bore and boundary tube to be exactly and reproducibly aligned. The boundary tube was similar to that used in the rising boundary cell (III 3. 4.1), and the anode and cathode resembled those used in the rising boundary cell. In most cases the cathode was placed in compartment B as shown and the anode in E, which would allow use of falling cation boundaries. For falling anion boundaries the anode was fitted onto a stout platinum wire mounted on a ground glass joint and placed in compartment B, the Ag/AgCl cathode in E.

The boundary tube and other electrode compartments were of similar dimensions to those described for the rising boundary cell.

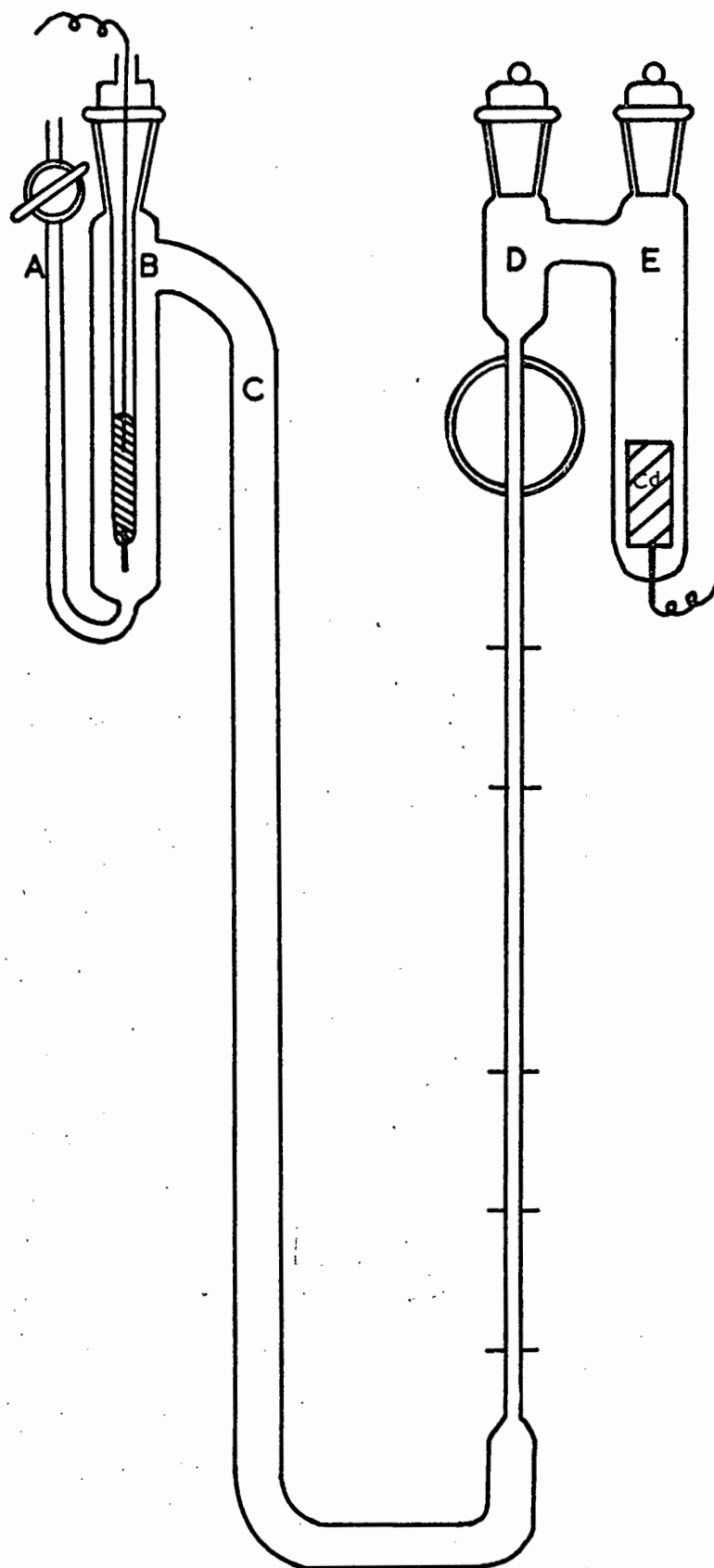


Fig. 24. Falling boundary cell.

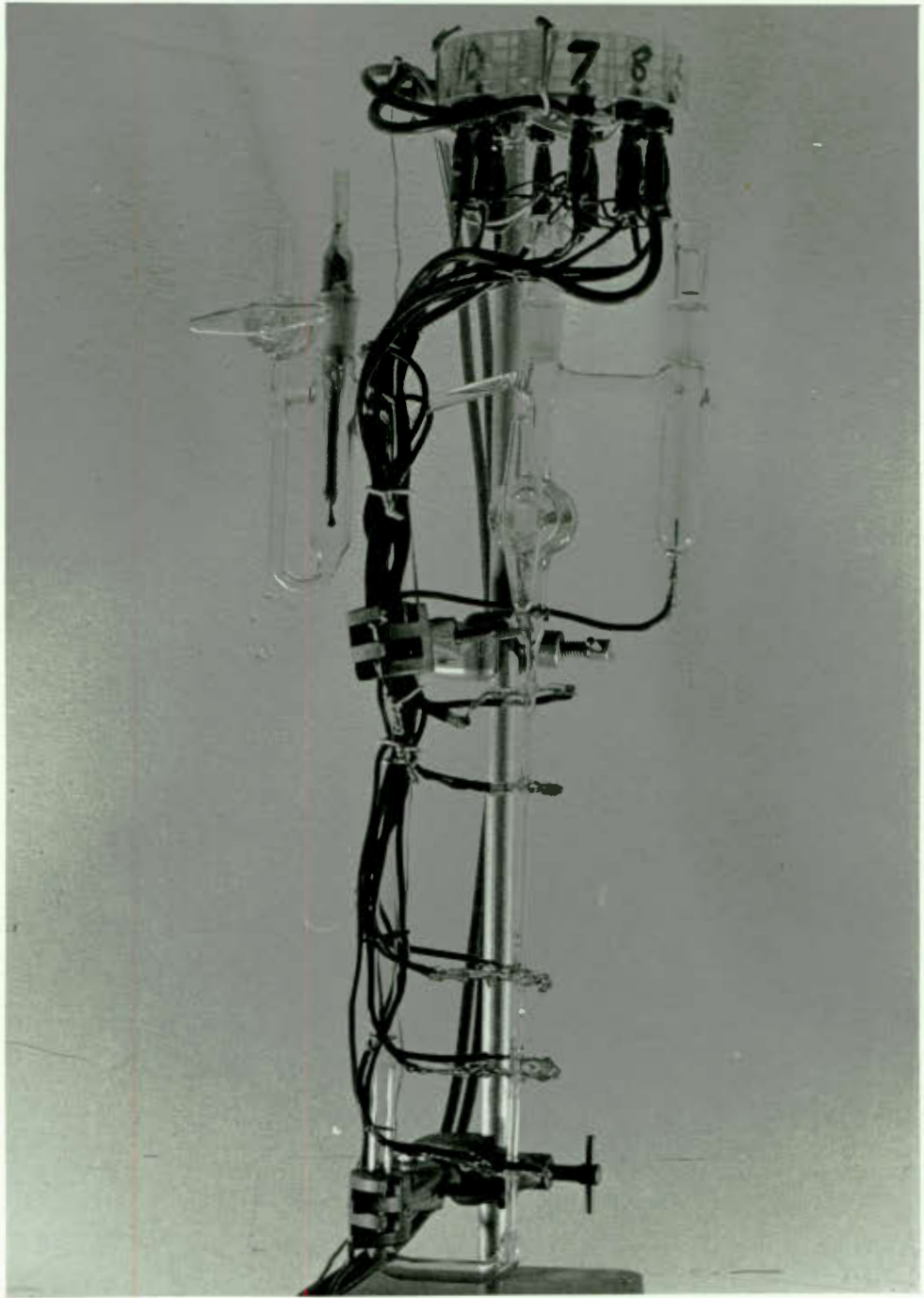


Fig. 25. Falling Boundary Cell.

Electrode pairs were numbered 1 to 5 down from the shearing stop-cock. The distance from plane S to the 1st pair was about 7 cm., and the narrow boundary tube extended about 2 cm. below the 5th pair. Compartment D was 0.5 cm. diameter and 2 cm. high. Construction details involving coaxial cables, fibre-glass resin support and insulation, perspex ring and phone tip sockets were similar to those described previously, and can be seen in figure 25. Operational procedures will be described in part IV. 5.

IV. 4 Preparation of the Salts and Solutions.

The solvent purification has been described in part II. The solutions were prepared by weight as described in part III 4.1 from salts prepared and purified as described below. Solutions in acetone were prepared in an atmosphere of dry nitrogen in a dry box. (II. 1)

All purified salts were stored in desiccators over silica gel and phosphorus pentoxide.

4.1 Purification of Inorganic Salts.

Potassium chloride: Johnson Matthey Specpure material was dried at 250° for 40 hours.

Sodium chloride: Johnson Matthey Specpure material was dried at 250° for 40 hours.

Lithium chloride: This salt was purified and dried as described in part III. 3. 1.3.

Potassium iodate: B.D.H. Analar reagent was recrystallised five

times from conductivity water and dried in vacuo over phosphorus pentoxide at 100° for eight hours.

Potassium iodide: Riedel de Haen Analar material was recrystallised four times from conductivity water and dried in vacuo over phosphorus pentoxide at 100° for eight hours.

Potassium Thiocyanate: B.D.H. Analar material was recrystallised three times from conductivity water and dried in vacuo over phosphorus pentoxide at 56° for 32 hours.

Lithium Bromide: B.D.H. laboratory reagent was recrystallised five times from distilled and conductivity water and dried in vacuo over phosphorus pentoxide at 100° for 24 hours.

4.2 Organic Materials - Preparation and Purification.

Bu_4NBr : Fluka 'purum' material was reprecipitated twice from Analar acetone solution with Analar ether and then twice recrystallised from a mixture of peroxide free Analar ether and Analar ethyl acetate. It was dried in vacuo over phosphorus pentoxide at 56° for 24 hours, m.p. $117.5 - 118.0^{\circ}$.

Bu_4NI : B.D.H. laboratory reagent was recrystallised five times from Analar petroleum ether ($100 - 120^{\circ}$) and the minimum amount of Analar ethanol and acetone. The crystals were dried in vacuo over phosphorus pentoxide at room temperature for 48 hours, m.p. $145.8 - 146.1^{\circ}$. The salt analysed at 99.99% pure.

Bu_4NCl : Fluka 'pract' reagent was precipitated five times from acetone with ether and dried in vacuo over potassium

hydroxide at 56° for two days. The purity as found by analysis was 99.98%.

Potassium picrate: KPic was prepared from stoichiometric amounts of Analar potassium hydroxide and picric acid dissolved in the minimum amount of hot conductivity water. The picrate which crystallised on cooling was filtered off and washed with Analar ethanol, followed by four recrystallisations from 50% aqueous ethanol. The salt was dried in vacuo over phosphorus pentoxide at 56° for 12 hours. The salt was analysed for N, C, H which were within 0.02% of the theoretical values.

Bu₄NPic: Tetrabutylammonium picrate was prepared from Bu₄NOH and picric acid in aqueous solution according to Fuoss.¹⁰⁴ The Bu₄NOH was prepared as described below. Silver hydroxide was prepared by reaction of the stoichiometric quantities of Analar silver nitrate and potassium hydroxide in aqueous solution, the precipitated silver hydroxide being filtered off. 12g of this AgOH were added to a solution of 20g of Bu₄NI in 50% aqueous ethanol, and the AgI formed and excess AgOH were filtered off, the filtrate being retained. The filtrate was mixed with a solution of 12.7g Analar picric acid in 50% aqueous Analar ethanol and the yellow crystals of Bu₄NPic obtained were recrystallised four times from 50% aqueous Analar ethanol and dried in vacuo over phosphorus pentoxide at about 40° for 24 hours. M.p. $88.6 - 89^{\circ}$. The salt analysed at 100.01% pure.

$\text{Na}_2 \text{C}_{20} \text{H}_6 \text{O}_5 \text{I}_4 \cdot \text{H}_2\text{O}$: The disodium salt of tetraiodofluorescein, (erythrosin) was made essentially according to the procedure described by Gomberg and Tobern.¹⁰⁵ The red crystals initially obtained are not pure erythrosin, but contain solvent of crystallisation both alcohol and water. In order to obtain the completely monohydrated salt the crystals were heated for 1 hour at 130° to remove the alcohol, dissolved in conductivity water and the solution evaporated to dryness in a rotary evaporater. The monohydrate was further dried under reduced pressure over phosphorus pentoxide at 100° for 8 hours, and tested for purity.¹⁰⁵ The water molecule is in fact too strongly held to be water of hydration and the structure is accepted as a hemiquinoid one.

IV. 5 Calibration of the Cells.

The volumes between pairs of microelectrodes were calibrated using the known transport numbers of aqueous potassium chloride solutions.^{93,108}

Initial experiments with the rising boundary cell yielded no results, and it was found advantageous to test the functioning of the apparatus by means of a visible boundary which would enable location of any fault. Hence it was decided to use the easily visible boundary formed between NaCl and the red erythrosin¹⁰⁷ as a trouble shooting step. For this case 0.01 M NaCl and 0.0078 M erythrosin were used in aqueous solution. The transport number used for 0.01 M NaCl was that determined by Longworth,¹⁰⁸ namely $t_{\text{Cl}^-}^{0.01 \text{ NaCl}} = 0.6082$.

These experiments showed that a stable boundary could be formed in the cell and that the constant current device was working satisfactorily. The fault was therefore located in the A.C. detector. Future workers are recommended to use this method for location of faults.

5.1 The Rising Boundary Cell.

The transport number used to calibrate this cell was the value
 $t_{Cl^-}^{0.01 \text{ KCl}} = 0.5098$ for 0.01 M KCl in aqueous solutions.^{93,108}

The leading solution was 0.01 M KCl with 0.0069 M KIO_3 as indicator solution. The experimental procedure will be described with reference to figure 22. In this figure the cell is shown with the shearing stop-cock in the 'run' position. Rotation of the stop-cock 90° anti-clockwise will bring it to the "fill" position. The same stop-cock settings were always used for all experiments. With the stop-cock in the fill position, and the anode inserted, compartments D, E and F were filled through D with the leading KCl solution and A, B and C with the KIO_3 indicator solution. The cathode was inserted, the anode having been positioned before filling, and the cell was closed with the four stoppers shown.

Prior to commencing a run a number of pre-run checks were always made. Electrical contacts were checked with an Avometer and leakage resistance with a megohmmeter. The oil in the thermostat tank was equilibrated at 25.00° and the cell placed in the tank. Stoppers in A and F were momentarily released to

allow for liquid expansion. The first electrode pair (nearest the stop-cock) were plugged into their phone tip sockets, all other electrodes being left unconnected and not touching each other or the stand holding the cell. The potentiometer was standardised against the standard cell and the current flowing through the dummy resistor D (fig. 19) was measured and adjusted to about 0.3 mA. The A.C. detector was switched to cell resistance, R_c , with switch S_1 (fig. 21) and the oscillator power control, detector sensitivity and scale controls R_1 and R_{10} adjusted to optimum settings. This adjustment was performed starting with the scale control, R_{10} , at a low value which meant a small voltage was measured by the Texas recorder, R , to prevent possible damage to it due to an initial recorder input signal $\gg 1$ mV. The optimum settings were those which gave a recorder deflection approximately 95% of f.s.d. with a minimum oscillator power output, minimum sensitivity setting on R_5 , and a resulting maximum scale control setting on R_{10} . As the boundary passed the first electrode pair, R_c would increase, since the conductance of, for example, 0.0069 M KIO_3 is less than that of 0.01 M KCl and hence the input signal reaching the recorder would decrease.

Once the recorder signal had been adjusted dummy, R_{11} , was switched in again with S_1 and R_{11} was adjusted to give the same recorder signal as just obtained with R_c . By this means the detection device was 'warmed up' on a resistance equal to that to be monitored at the start of the experiment.

After one hour in the thermostat the electrical checks were repeated and the A.C. detector switched to monitor R_c (switch S_1 , fig. 21). The shearing stop-cock was rotated 90° clockwise and carefully aligned to the marks referred to in (IV 3. 4.1). The current was switched to cell (switch W, fig. 19) immediately before shearing the boundary in plane S (fig. 22). During a run the cathode side, C, was kept open to the atmosphere by inserting a length of platinum wire between the male and female parts of the ground glass joint holding the cathode. This ensured that volume corrections (IV. 6) were only required for the reactions occurring at the anode. All other stoppers were tightly closed.

The Texas recording millivoltmeter, R, was run with a chart speed of 6" per hour until it was estimated that the boundary was approaching pair 1, whereupon it was run at 6" per minute till after the boundary had passed the fifth pair. Time was measured by means of this recorder, the chart speed being calibrated and frequently checked against a Dent chronometer. The chronometer was calibrated against accurate time signal 'pips' from the South African Broadcasting Corporation. As the boundary passed the pair of micro-electrodes the signal recorded decreased, giving a curve similar to that shown in figure 26, which is a trace for 0.0099317 M KCl followed by 0.006912 M KIO_3 with a current of 0.3656mA. The important quantity measured is the time taken for the boundary to move from one electrode pair to the next. Hence, to measure this

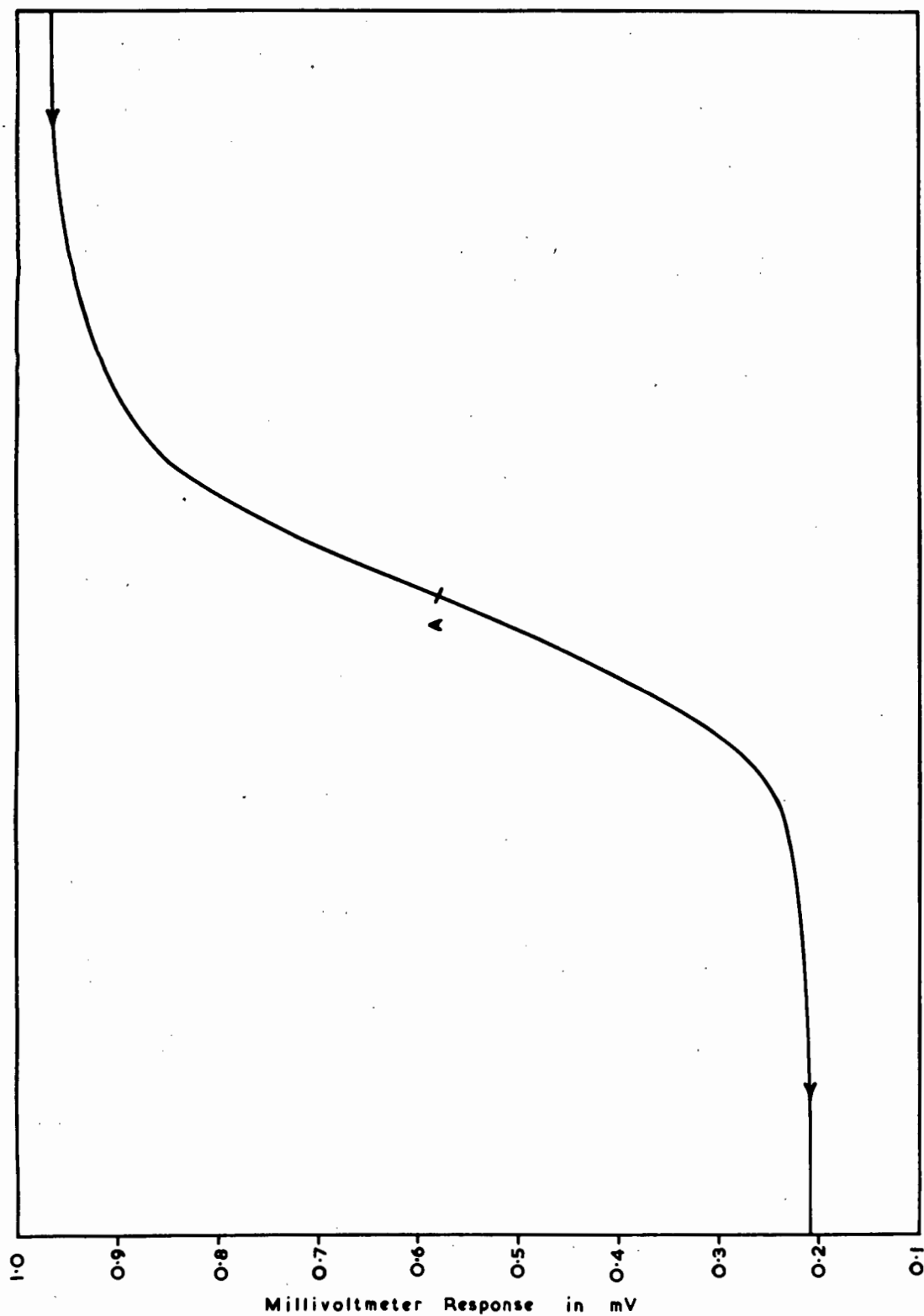


Fig. 26. Trace on recording millivoltmeter for passage of an approximately 0.01M KCl/0.0069M KIO_3 boundary with a current of 0.3656 mA flowing.

interval some point on this trace must be used as corresponding to the 'event'; the boundary being of finite thickness,¹⁰⁷ as are the electrodes. The point used was the point of inflection of the curve, point A, which is the average of the signals when only leading or indicator solution was between the electrodes. By this means time could be determined to within ± 0.2 seconds. The total time for the boundary to travel from electrode pair 1 to 5 was more than an hour. The pairs of electrodes were successively plugged in one pair at a time as the boundary progressed up the tube. After completion of an experiment, the thermostat oil was thoroughly rinsed from the cell with acetone and carbon tetrachloride and the cell cleaned, filled with 40% R.B.S. 25, and left overnight, followed by prolonged rinsing with conductivity water, A.R. methanol, A.R. acetone and finally A.R. carbon tetrachloride. The cell was dried with a stream of dry nitrogen.

Current was measured every 90 seconds and a current-time plot integrated using a planimeter to find the total number of coulombs passed.

The data were corrected for solvent conductance,¹⁰⁷ and volume changes¹⁰⁷ at the closed cadmium anode using the equation

$$t_{\text{correct}} = t_{\text{observed}} \left(1 + \frac{\kappa_{\text{solvent}}}{\kappa_{\text{solution}}} \right) - \frac{C \Delta V}{1,000}$$

where κ_i is the specific conductance of i

κ_{solvent} was $1.01 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and κ_{solution} at the

concentrations used was calculated from the equation of Fuoss⁴⁵ et al.

The volume correction was $-C\Delta V/1000$ where

$$\Delta V = t_+ \bar{V}_{KCl} + \frac{1}{2}V_{Cd} - \frac{1}{2}\bar{V}_{CdCl_2} \quad \text{where}$$

V_{Cd} is the molal volume of cadmium^{106,107} and

\bar{V}_{CdCl_2} , \bar{V}_{KCl} are the partial molal volumes¹⁰⁷ of those salts in aqueous solution at the concentrations used. ΔV is the volume change for the passage of 1 Faraday.

The volume between microelectrodes in cm^3 , v , was found from the equation¹⁰⁷

$$v = \frac{10^3 \times t_{Cl^-} \times 0.01KCl \times i \times t}{c \times F}$$

where i is the current in amperes, t the time in seconds, c the molarity and F the Faraday. Six such calibrations were made for this cell spread over the duration of the work. The average volumes found are shown in Table 14, and a standard deviation of 0.04% was obtained.

TABLE 14.

VOLUME CALIBRATION OF RISING BOUNDARY CELL.

Electrode pair intervals	Volume, v , cm^3
1 - 2	0.22196
2 - 3	0.20931
3 - 4	0.44031
4 - 5	0.22607

5.2 Calibration of the Falling Boundary Cell.

The volumes between microelectrodes were calibrated using

$$t_{K^+}^{0.01 \text{ KCl}} = 0.4902 \quad \text{as the transport number}^{93,108} \quad \text{for } K^+$$

in 0.01 M KCl.

The leading solution was ca. 0.01 M KCl and the indicator solution was 0.0078 M NaCl, the indicator concentration being calculated from the Kohlrausch ratio. The experimental procedure will be described with reference to figure 24.

The shearing stop-cock in figure 24 is open and rotation through 90° will close it. With both the stop-cocks open and the cadmium anode inserted the leading 0.01 M KCl solution was run in through compartment B to fill A, B, C and D to a level just above plane S. The shearing stop-cock was then closed and A and B were filled to the top with KCl solution, whereupon the cathode was inserted and the side-arm stop-cock in A was closed. The few drops of KCl in compartment D just above the stop-cock were removed with a fine capillary dropping pipette. Compartment D was thoroughly flushed with the NaCl indicator solution using the pipette and D and E were then filled with indicator solution.

The first electrode pair (nearest the stop-cock) were connected to phone tip sockets and after the electrical contact and resistance checks had been made, as for the rising boundary cell, the cell was placed in the thermostat which was already at 25.00° . The

cathode and stopper, E_1 were momentarily opened to allow for expansion of liquid, the constant current device and A.C. detector were adjusted as described for the rising boundary (R.B.) cell and the cell was left in the thermostat for an hour at 25.00° , the electrical devices being warmed up on their respective 'dummy' resistors.

After an hour the electrical checks were repeated, the constant current switched to cell (switch W, fig. 19), the shearing stop-cock carefully opened and the detector switched to cell (switch S_1 , fig. 21). During a run the cathode was kept open with a length of platinum wire to confine volume corrections¹⁰⁷ to the closed anode compartment. As the boundary progressed down the tube successive pairs of electrodes were plugged in on the Perspex ring. The boundary curves obtained were similar to those obtained for the R. B. cell (fig. 26) and time intervals and current were measured as described previously (IV. 5.1). After each experiment the cell was thoroughly cleaned inside and outside with organic solvents and water, and soaked overnight filled with 40% R.B.S. 25, followed by careful and thorough rinsing with distilled and conductivity water, Analar methanol, acetone and carbon tetrachloride and dried with a stream of dry nitrogen.

Solvent and volume corrections^{106,107} were applied to the data and volumes calculated. The results are shown in Table 15 with a precision of $\pm 0.05\%$ for the four determinations made during the work.

TABLE 15.VOLUME CALIBRATION OF FALLING BOUNDARY CELL

Electrode Pair Intervals	Volume, v , cm^3
1 - 2	0.17848
2 - 3	0.36514
3 - 4	0.18706
4 - 5	0.19421

IV. 6 Transport Measurements in Anhydrous Acetone.6.1 Introductory Theoretical Considerations.

Very recently Spiro⁸¹ has shown that when dealing with incompletely dissociated electrolytes in transference work, it is important to consider not the ions but the ion constituents. An ion constituent is the ion-forming portion of an electrolyte without reference to the extent to which it may actually exist in the dissociated state.¹⁰⁹

The transference number, t_x , of an ion constituent X is defined¹⁰⁹ as the net number of gram equivalents of X crossing an imaginary plane in the solution fixed with respect to the solvent, in the direction of the cathode for a cation constituent (Z_x positive) and in the direction of the anode for an anion constituent (Z_x negative), when one faraday of electricity passes across the plane.

A number of misconceptions in the literature regarding transference in weak electrolyte solutions have recently⁸¹ been corrected. Equations governing the motion of the boundary between two weak electrolytes and the conditions for boundary stability have been derived⁸¹ and the importance of using the above definitions has been shown.^{81,109} The fundamental moving boundary equation has been derived by MacInnes and Longworth in a classical paper¹⁰⁷

$$t_{\pm} = \frac{v c F}{1000 i t} \quad \dots 6.1.1$$

where c is the normality of leading solution, $v \text{ cm}^3$ the volume "swept through" by the boundary between leading and indicator solution with a current i amperes flowing for t seconds.

Certain electrochemical criteria must be satisfied before a stable boundary is obtained. The leading solution must be more dense than the following for falling boundaries, and less dense for rising, otherwise mixing would occur immediately. Let superscript l denote leading solution and i denote indicator solution. The Kohlrausch ratio¹⁰⁷ gives the concentration, c_Y^i , to which the indicator electrolyte adjusts itself behind a moving boundary when a stable boundary has been formed. The ratio is

$$\frac{c_X^l}{c_Y^i} = \frac{t_X^l}{t_Y^i} \quad \dots 6.1.2$$

where t is the transport number and X and Y are the non-common ion constituents of the leading and indicator solutions respectively. The initial indicator concentration, $c_Y^{i'}$, used must be within a few per cent of the adjusted value, c_Y^i , if the correct value of t_X^1 is to be obtained. In water at 25° , $c_Y^{i'}$ can differ from c_Y^i by up to about 40% for a rising boundary.⁹³ At 45° the difference can be only about 1% if accurate results are to be obtained. The reason why the adjusted indicator concentration c_Y^i does, in general, differ from $c_Y^{i'}$ is really because at the boundary Y must move at the same rate as X , which can only occur at one concentration for a given c_X^1 . The variation of t_{\pm} with indicator concentration has been mentioned by MacInnes and Longworth¹⁰⁷ and by Gordon and co-workers.⁹³ Their results, for LiCl/KCl and KIO_3/KCl boundaries at 25° and 45° respectively, differ considerably, but it is clear that there is only a limited range for $c_Y^{i'}$ outside of which incorrect results are obtained.

The initial indicator concentration, $c_Y^{i'}$, has been shown to adjust itself up⁹⁴ or down⁸⁴ to the adjusted value, c_Y^i and MacInnes and Longworth¹⁰⁷ have stated that falling boundaries are more sensitive to an initially incorrect indicator concentration than rising ones, but more recently Gordon and Kay⁹⁴ disprove this in certain, if not all, cases. Current workers^{26,94,117} favour using an initial $c_Y^{i'}$ about 3% below the theoretical c_Y^i calculated from the Kohlrausch ratio, equation 6.1.2, for falling

boundaries and about 3% above for rising. Transport numbers for use in equation 6.1.2 must be estimated (in the light of any available information) initially and after a few trial experiments the correct c_Y^i to use can be found. When dealing with incomplete dissociation, as in this work, it is vital to note that the concentrations involved are those of ion constituents, and thus stoichiometric ones and not the concentrations of ions.

The boundary between solutions i and l will only be stable^{81,107} if leading ion constituent X that enters solution i moves faster than the boundary, and if the boundary itself is moving faster than Y . This stability condition can be expressed⁸¹ in terms of the mobilities of ion constituents \overline{u}_X , \overline{u}_Y by

$$\frac{\overline{u}_X^i}{\overline{u}_X^l} > \frac{\overline{u}_Y^l}{\overline{u}_Y^i} \quad \dots 6.1.3$$

$$\frac{\overline{u}_X^i}{\overline{u}_X^l} > \frac{\overline{u}_Y^i}{\overline{u}_Y^l} \quad \dots 6.1.4$$

Spiro⁸¹ has shown that for a boundary between two weak electrolytes, $RA \leftarrow RB$, where RA is the leading solution, and using concentration equilibrium constants, K , defined by

$$K_{RA} = \frac{c_{R^+} c_{A^-}}{c_{RA}} \quad \dots 6.1.5$$

and the fact that the mobility of molecular species RA and RB is zero, the general conditions 6.1.3 and 6.1.4 lead to

$$\frac{u_{A^-} K_{RA}}{c_{R^+} K_{RA}} > \frac{u_{B^-} K_{RB}}{c_{R^+} K_{RB}} \quad \dots 6.1.6$$

in the leading or indicator solutions. In the above four equations u_{A^-} , u_{B^-} , the mobilities of ions A^- , B^- , are related to the mobilities of the ion constituents \bar{u}_{A^-} , \bar{u}_{B^-} by

$$\bar{u}_{A^-} = \frac{u_{A^-} c_{A^-}}{c} \quad \dots 6.1.7$$

where c_{A^-} is the normality with respect to ion A^- and c the normality of the solution.

A special case of equation 6.1.6 occurs when both RA and RB are so weak that

$$c_{R^+} \gg K_{RA} \quad \text{and} \quad c_{R^+} \gg K_{RB} \quad \dots 6.1.8$$

Equation 6.1.6 then simplifies to give

$$u_{A^-}^1 \times K_{RA}^1 > u_{B^-}^1 \times K_{RB}^1 \quad \dots 6.1.9 a$$

$$\text{and} \quad u_{A^-}^i \times K_{RA}^i > u_{B^-}^i \times K_{RB}^i \quad \dots 6.1.9 b$$

If both electrolytes are completely dissociated the stability condition becomes, from 6.1.6

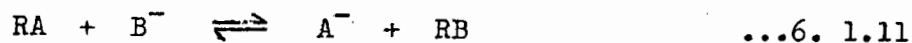
$$u_{A^-}^i > u_{B^-}^i, \quad u_{A^-}^1 > u_{B^-}^1 \quad \dots 6.1.10$$

which is the familiar¹⁰⁷ condition stating that the leading ion must have a higher mobility than the following non-common ion in both leading and indicator solutions. However, as 6.1.9 shows,

this simple condition only holds for completely dissociated electrolytes. A third special case, when only one of RA or RB is weak, will not concern work in acetone or water described in this thesis.

Equations 6. 1.9a,b thus show that an indicator RB will form a stable boundary with a leading solution, RA, even if the following ion B is faster than the leading ion A, provided the electrolyte RB is sufficiently less dissociated than RA.

In strong electrolyte solutions the only restoring effect¹⁰⁷ which overcomes disturbing effects at the boundary caused, for example, by diffusion, is the greater potential drop present in the poorer conducting following solution than in the leading one. Equation 6. 1.9 shows this potential effect will also hold in weak electrolyte solutions, but in these cases an association effect will also assist in maintaining a stable boundary. The fact that K_{RA} and K_{RB} are different in magnitude will cause the mobility of an ion constituent to change as it crosses the boundary by a reaction such as



In other words any B^- ions that enter the leading solution are converted into RB molecules and are eventually passed by the moving boundary, and any molecules of RA that are left behind as the boundary advances react according to equation (6. 1.11) and A^- ions formed overtake the boundary and re-enter the leading solution. The electrochemical stability conditions discussed above are not the

only ones and the absence of vibration, convection and Joule heating¹⁰⁷ is also essential.

6.2 Trial Measurements and Discussion.

The brief considerations of the previous sub-section (IV. 6.1) served to indicate what criteria governed the choice of systems (leading and following solutions) for moving boundary measurements in acetone.

For the first trials, equation 6. 1.9 was used to govern the initial choice of possible moving boundary systems. Once a system had been selected the initial indicator concentration for a certain leading concentration could be selected by the Kohlrausch rule, equation 6. 1.2. It can be seen from 6. 1.2 that selection of c_Y^i requires knowledge of t_X^1 and t_Y^i , both of which are unknown. To assist in this problem, the very approximate (see IV. 7) limiting conductances calculated by the method of Fowler and Kraus¹¹⁰ were used. This method involves the assumption that large ions of a few particular salts, such as $Bu_4N^+ Ph_3 BF^-$, have identical limiting ionic conductances. That this equivalence is only very approximate is clear from the discussion of specific ion-solvent interaction in III. 6 and (see later) IV. 7, since it assumes a large cation (Bu_4N^+) and large anion ($Ph_3 BF^-$) have identical ion solvent interactions, if any. Kraus⁸ value of $134.2 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ for the limiting ionic conductance of $(n-Bu)_4 N(C_6H_5)_3 BF$ was used to give a value of $\lambda_o^+ \sim 67.1$ for $(n-Bu)_4 N^+$. The conductances of several $(Bu)_4 N^+$ salts have been measured in

acetone,^{8,10} and using the above value approximate limiting ionic conductances could be evaluated for several ions.

For Bu_4NPic , $K_D = 0.0223$ and $\lambda_o^+ \sim 67 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ which suggested that this salt could be used in a leading solution followed by KPic which has $K_D = 0.00343$ and $\lambda^+ \sim 80.6 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$.

This was the first system tried, the falling boundary cell being used with a leading concentration of

$$c_{\text{Bu}_4\text{NPic}} = 0.00798 \quad \text{and} \quad c_{\text{KPic}} = 0.00849$$

However, a stable boundary was not obtained. The two solutions interdiffused within a few seconds. The first four systems shown in Table 16 all failed to give a stable boundary.

TABLE 16 ...

TABLE 16.
TRANSFERENCE SYSTEMS IN ACETONE.

System Number	Leading Solution	Leading conc., M	Indicator Solution	Indicator conc., M	Approximate values of	
					$\lambda_o^l K^l$	$\lambda_o^i K^i$
1	Bu ₄ NPic	0.0079	KPic	0.006 to 0.010	1.39	0.26
2	Bu ₄ NPic	0.0080	Bu ₄ NBr	0.006 - 0.010	2.01	0.40
3	Bu ₄ NBr	0.0088	Bu ₄ NPic	0.006 - 0.010	121.8(λ_o)	90.2 (λ_o)
4	KI	0.003 to 0.010	Bu ₄ NI	0.001 - 0.009	0.61	0.40
5	KI	0.005 - 0.010	KPic	0.0038 - 0.0094	0.97	0.31
6	KI	0.0010-0.0046	KPic	0.00077-0.00450	0.97	0.31
7	Bu ₄ NI	0.0020	Bu ₄ NBr	0.0019 - 0.0024	0.78	0.40
8	KCNS	0.0011-0.0028	KPic	0.0008 - 0.0021	0.48	0.31
9	Bu ₄ NCl	0.0020	LiCl	0.0020 - 0.0026	0.10	0.002
10	Bu ₄ NBr	0.0020	LiBr	0.0020 - 0.0026	0.21	0.02

Concentrations used for leading and indicator solutions were in the ranges shown in columns 3 and 5 respectively. Columns 6 and 7 give approximate values of $\lambda_o K$ for the leading and indicator solutions respectively, thus constituting a test of equation (6. 2.1) (see below). In all cases λ_o values must be used,

since no transport data are available in acetone to give ionic conductances at various concentrations. The concentration equilibrium constants K were taken as being the dissociation constants found from the conductance data.^{4,8,3} The first, second, seventh, ninth and tenth boundaries were falling, the rest rising. For each leading concentration a range of indicator concentrations was used above and below the approximate value calculated from the Kohlrausch rule using the available conductance data. It should be noticed that the choice of systems was in fact such that

$$\lambda_o^{1K1} > \lambda_o^{iKi} \quad \dots 6. 2.1$$

$$\text{i.e. } u_A^{1-K1} > u_B^{i-Ki} \quad \dots 6. 2.2$$

due to the fact that the data for formulation of equations 6. 1.9 are unknown. Electrical mobility and ionic conductance are related by $\lambda = u F$ where F is the Faraday. It may be possible that the dissociation constant of Bu_4NPic , 0.0223, is too high, although other systems with much lower dissociation constants for the leading solutions, and low indicator K_D also failed to produce stable boundaries.

Since the second system shown in Table 16 failed, and because K_D for Bu_4NPic may have been too large, system 3 was tried since $\lambda^{\text{Br}^-} \sim 110 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ and $\lambda^{\text{Pic}^-} \sim 85$ which would satisfy equation 6. 2.1 if the equilibrium constants were ignored.

A number of trials were performed on the first four systems shown without a stable boundary being formed. In all cases diffusion occurred, more rapidly in the first three cases but more slowly in case 4. Diffusion was indicated by a long, slow (five minutes) signal drop on the recorder, and this suggested no true boundary was being formed at all. The system $KI \longleftrightarrow KPic$ (systems 5 and 6) was then tested and boundaries were obtained. For the concentration ranges shown in system five (0.005 - 0.01 M) the boundary was very unstable and never progressed further than the first electrode pair before becoming unstable. Possibly Joule heating at higher concentrations was the reason for this, because the concentration ranges for system 6 gave more stable boundaries.

The boundaries of system 6 gave consistent results, once the correct concentration ratios had been found, but were found to be very elongated; the time of the 'event' as the boundary passed an electrode pair being about three minutes and up to four minutes at the fifth electrode pair, with a current of 0.08mA. This phenomenon has been observed by Graham and Gordon⁸⁷ to a greater extent using $NaCl \longleftrightarrow LiCl$ cation boundaries in ethanol. No explanation can be offered in this case where an anion boundary is being used. Hence, although the results were as precise as could be expected from such long boundary curves, the $KI \longleftrightarrow KPic$ system was abandoned.

Measurements with Bu_4NI and Bu_4NBr gave no results in that diffusion occurred within a few minutes of starting the current,

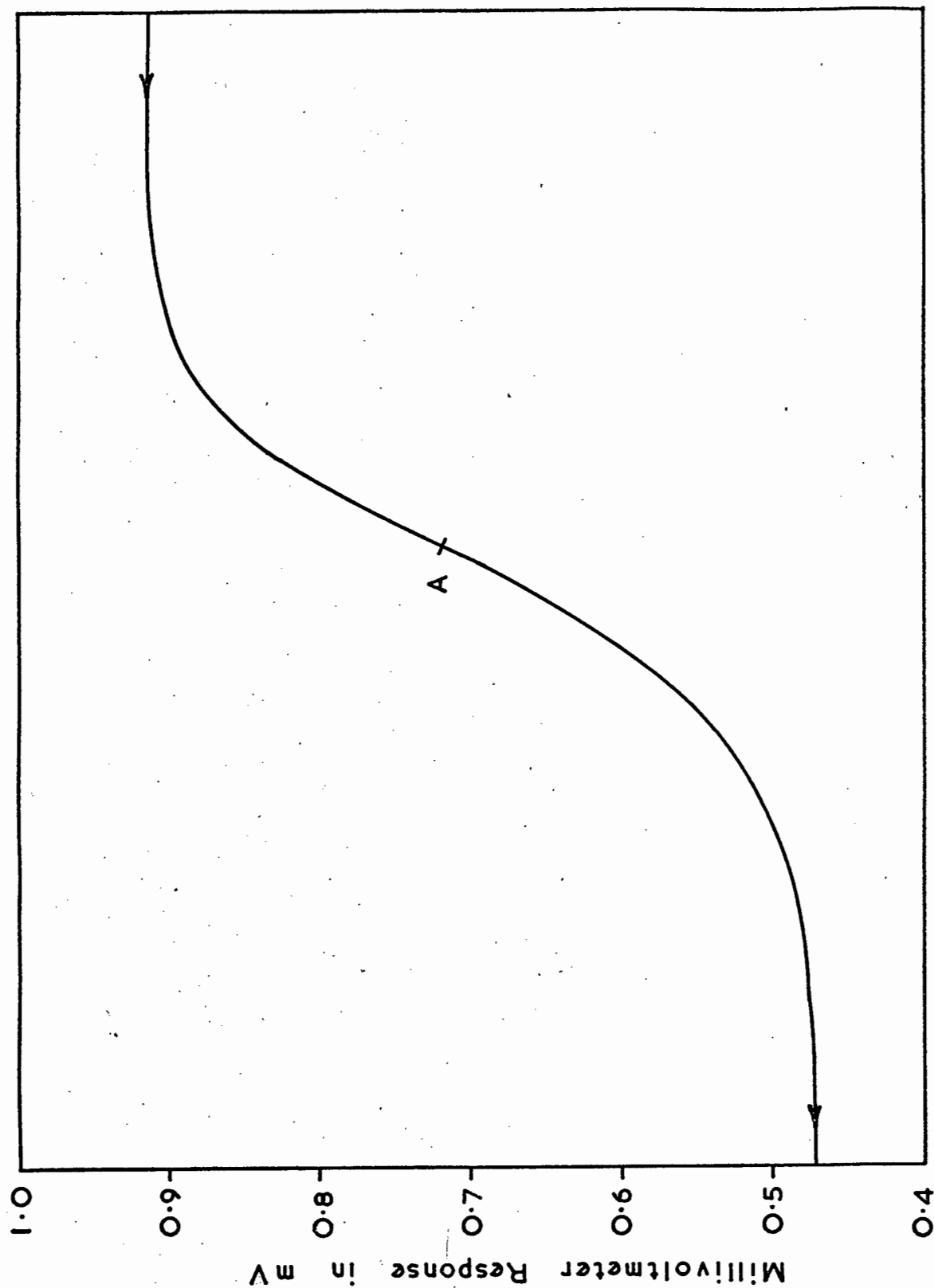


Fig. 27. Trace on recording millivoltmeter for passage of 0.001996M KCNS/0.001539M K picrate boundary past the second electrode pair with a current of 0.08877 mA flowing.

which was about 70 μ amp

Other workers, including Gordon and co-workers,^{87,89} Spiro⁸⁸ and Longworth¹⁰⁸ have also had difficulty in finding suitable systems for various reasons.

Potassium thiocyanate followed by potassium picrate (system 8) in the rising boundary cell gave excellent boundary curves, and results with a precision of $\pm 0.15\%$ for the transport number of (presumably) CNS^- in KCNS in acetone were obtained. A typical boundary curve is shown in figure 27. It is noteworthy that Table 16 shows that the difference between $\lambda_o^{\text{l}}\text{K}^{\text{l}}$ and $\lambda_o^{\text{i}}\text{K}^{\text{i}}$ for $\text{KCNS} \leftarrow \text{KPic}$ is in fact smaller than for any of the other systems tried. Details will be given in the following section.

Other attempts made are shown as systems 9 ($\text{Bu}_4\text{NCl} \leftarrow \text{LiCl}$) and 10 ($\text{Bu}_4\text{NBr} \leftarrow \text{LiBr}$) which gave no results for 9 and unstable boundaries for 10. System 9 did not form any detectable boundary at all, probably because of the extremely low dissociation constant of LiCl (2.9×10^{-6}) and correspondingly low conductance at finite concentrations, resulting in excessive Joule heating in the indicator solution. The results found in systems 5 and 6 suggested that low concentrations should be used (below ca. 0.005 M) and this was adhered to. Attempts 9 and 10 were made after attempt 8 in a further effort to obtain a cation transport number. No cation boundaries gave even the remotest indication of being stable, which resembles the findings of Graham and Gordon⁸⁷ on solutions in ethanol. They suggested that if cations are more highly solvated

than anions, as is probably the case in acetone (see III. 6.2 and IV. 7.2), a possible explanation is that the random passage of a cation across a cation boundary would produce a more serious disturbance than would the similar passage of an anion across an anion boundary particularly when density stability is slight, which is also the case in acetone.

IV.7 Results and Discussion.

The operation of the rising boundary cell for measurements with acetone was exactly as described for the aqueous calibration measurements in IV. 5.1, except that the cell was filled (with acetone solutions) in an atmosphere of acetone-saturated dry nitrogen in a dry box. Leading solutions were prepared by weight, and two series of transport measurements were obtained with each leading solution using indicator concentrations which differed by 4%. The first indicator solution was prepared by weight and for the second experiment, with the same leading KCNS solution, acetone was added to the reweighed flask containing the remaining KPic indicator solution so as to dilute it by 4%.

If the results from duplicate experiments did not agree satisfactorily, both sets of results were discarded, and similarly if the average result was not compatible with results at other concentrations. The anion transport numbers obtained were found to be independent of initial indicator concentration within a limit of 4%, independent of current within the limits shown, and did not vary significantly as the boundary moved up the tube. In other words

all internal criteria¹⁰⁷ for stable boundary formation were satisfied. The results are shown in Table 17.

TABLE 17.

ANION CONSTITUENT TRANSPORT NUMBER OF KCNS IN ACETONE.

$10^3 c^l, M$	$10^3 c^i, M$	$i, \mu A$	t_-	α	$10^3 \alpha c$	$t_-^{o'}$
1.1037	0.80	74 - 85	0.6346	0.8716	0.9620	0.6271
1.6238	1.19	85 - 97	0.6376	0.8422	1.3676	0.6283
1.9069	1.41	85 - 99	0.6390	0.8293	1.5813	0.6288
1.9957	1.48	86 -109	0.6393	0.8255	1.6475	0.6290
2.4351	1.81	85 -117	0.6415	0.8090	1.9701	0.6298
2.8145	2.10	87 -122	0.6432	0.7969	2.2429	0.6306

The molar concentration of the leading solution is shown in the first column, the average indicator concentration in the second column, the current range in the third, and the average value of t_- found in the fourth. Concentrations above about $2.8 \times 10^{-3} M$ were not used to prevent interference due to triple ion formation.⁴⁵ Below about 0.001 M the anode to cathode resistance became very high (greater than 5 megohm at 0.0006 M) and the results varied erratically as the boundary progressed up the tube. Graham and Gordon⁸⁷ found similar erratic variation with 0.0005 M NaCl in ethanol and ascribed it, in part, to turbulent electroosmotic flow, which may put a lower limit to the concentration at which moving boundary measurements are possible. In this work it is suggested that the reason may be excessive resistance heating⁸⁸ at such low concentrations (0.0006 M KCNS).

The t_- of column four was calculated from

$$t_- = \frac{v c F}{10^3 i t}$$

the meaning of the symbols being those given earlier (IV. 5.1) and corrected for solvent conductance using the equation¹⁰⁷

$$t_- = t_{\text{observed}} \left(1 + \frac{\kappa_{\text{solvent}}}{\kappa_{\text{solution}}} \right)$$

where $\kappa_{\text{solvent}} = 1 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ and κ_{solution}

was estimated from Reynolds and Kraus'⁸ results for the conductance of KCNS in acetone. Volume corrections cannot be calculated because the electrode reactions are unknown, and partial molal volumes in acetone are also unknown. However at the low concentrations used here volume corrections will be negligible⁸⁷ compared to the experimental error.

Five transport numbers were obtained from each experiment corresponding to the electrode pair intervals

$$1 - 5, 1 - 4, 2 - 5, 2 - 4, 3 - 5,$$

which gives a minimum boundary traverse of 12 cm. The smaller intervals 1 - 2, 2 - 3, 3 - 4, 4 - 5 were only used to check on the consistency of the results as the boundary progressed up the tube. The precision of the ten values obtained from the duplicate experiments, expressed as the range about the mean, was 0.15%.

The limiting transport number, $t_{\text{CNS}^-}^0$, was found using the

Longworth function,¹⁰⁸ $t_{-}^{o'}$, computed on the basis of ionic concentration in order to take account of association:

$$t_{-}^{o'} = \frac{t_{-}\Lambda' + \beta(\alpha c)^{\frac{1}{2}}}{\Lambda' + 2\beta(\alpha c)^{\frac{1}{2}}}$$

$$\text{where } \Lambda' = \Lambda_0 - (\alpha'\Lambda_0 + 2\beta)(\alpha c)^{\frac{1}{2}}$$

where α = degree of dissociation

$$\alpha' = \frac{8.204 \times 10^6}{(\epsilon_r T)^{\frac{3}{2}}} = 1.72058$$

$$\text{and } \beta = \frac{41.25}{(\eta \epsilon_r T)^{\frac{1}{2}}} = 173.689$$

c = molar concentration of KCNS

$$\text{and } \Lambda_0 = 201.6 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}.$$

The conductance of KCNS in acetone at 25° has been measured by Reynolds and Kraus⁸ and by Sears, Wilhoit and Dawson.¹¹¹

The former authors found $\Lambda_0 = 201.6 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ and

$K_D = 3.83 \times 10^{-3}$ and the latter $\Lambda_0 = 201.6$, $K_D = 3.4 \times 10^{-3}$.

The former authors used $\epsilon_r = 20.47$, the latter 20.7.

The value of $K_D = 3.83 \times 10^{-3}$ was used in this work for calculation of α as follows:

The limiting law activity coefficient, f , is given by¹⁰

$$\log f = A (\alpha c)^{\frac{1}{2}}$$

$$\text{where } A = \frac{1.8246 \times 10^6}{(\epsilon_r T)^{\frac{3}{2}}} = 3.8269 \text{ for acetone at } 25^\circ \text{ C.}$$

$$\text{Also } K_D = f^2 \alpha^2 c / 1 - \alpha \quad \text{and hence}$$

$$\log \frac{K_D (1 - \alpha)}{\alpha^2 c} = 7.6538 (\alpha c)^{\frac{1}{2}}$$

This non-algebraic equation was solved for α at the values of c in Table 17, using Newton's iteration formula¹¹² and carrying out the calculations using an I.C.T. 1301 computer, with an initial value of $\alpha = 0.75$ being used. The α values thus found are shown in column 5 of Table 17. A plot of t_-^0 (column 7) was found to be linear in αc (column 6), (Fig. 28), within the experimental error of the results, thus permitting an unambiguous extrapolation by least squares analysis to infinite dilution to obtain t_-^0 .

Once $t_{\text{CNS}^-}^0$, the limiting anion constituent transport number at infinite dilution for KCNS, is known, the limiting ionic conductances may be obtained from the limiting equivalent conductance of KCNS, for which identical values (201.6) have been obtained by both Reynolds and Kraus⁸ and by Sears, Wilhoit and Dawson.¹¹¹

The ionic conductances are

$$\begin{aligned}\lambda_{\text{CNS}^-}^0 &= 125.9 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1} \\ \lambda_{\text{K}^+}^0 &= 75.7 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}\end{aligned}$$

as calculated from $t_{\text{CNS}^-}^0 = 0.6244 \pm 0.0009$.

Assuming Kohlrausch's law is valid the limiting ionic conductances of many ions in solution may be calculated. Table 18a gives limiting ionic conductances in acetone at 25°, calculated from the conductance data of this work, Kraus and co-workers,^{4,8} Dippy

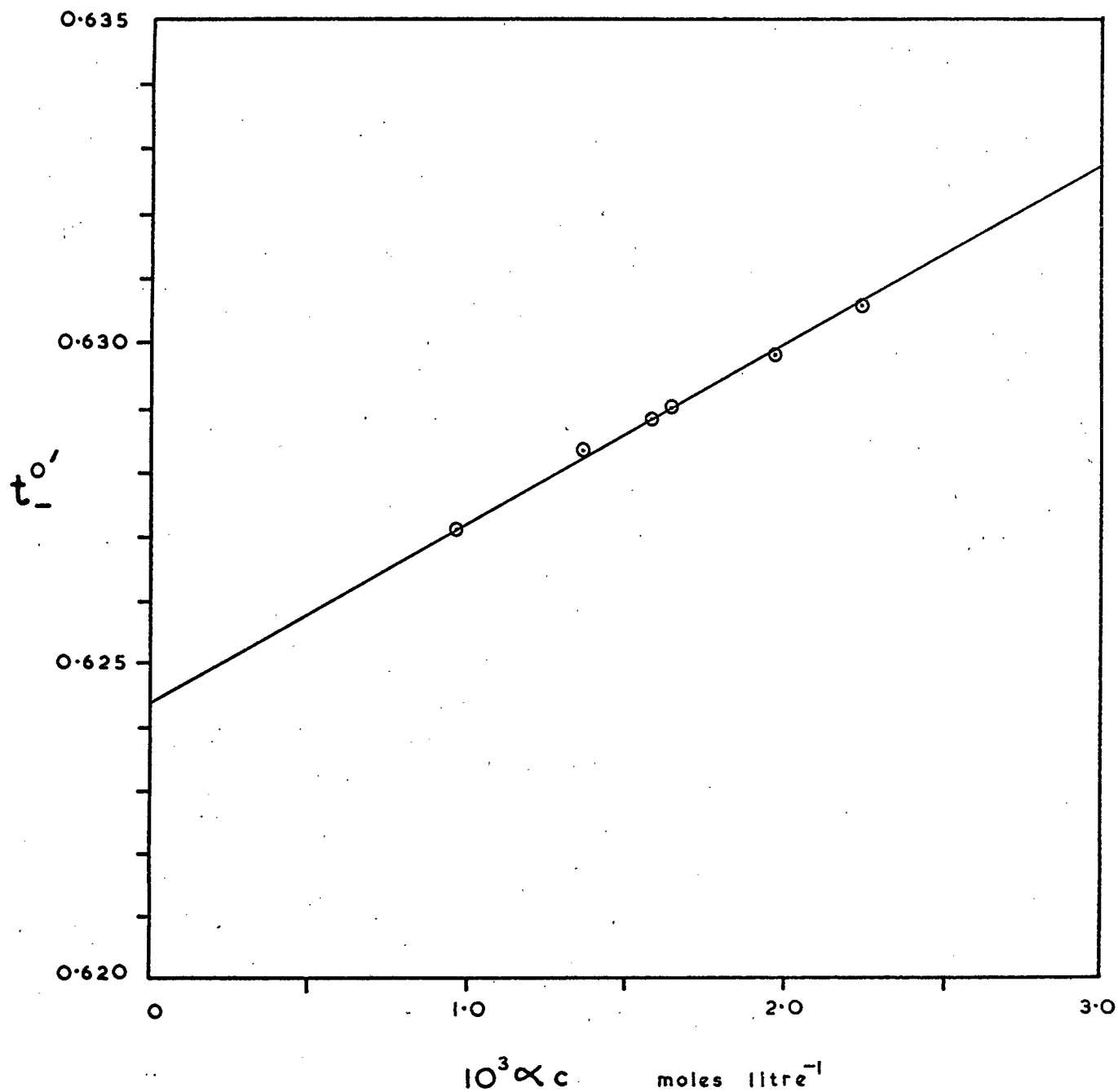


Fig.28. Plot of Longworth function against αc for the anion constituent of KCNS in acetone.

and Hughes,³ Savedoff,¹⁴ Sears, Wilhoit and Dawson,¹¹¹ and Accascina and Schiavo.¹¹ In all cases the ionic conductances calculated from the conductance data of different workers disagree by more than the combined experimental error (where quoted) of such workers. This suggests that if more precise values are required, much of the conductance work in acetone should be repeated. As an example, the limiting ionic conductance of the chloride ion as found from Bu_4NCl is 109 as found from Kraus,⁴ Λ_0 value of 172, and 125 as deduced from Savedoff's¹⁴ Λ_0 value of 188. However Kraus⁷¹ has mentioned that his Λ_0 for Bu_4NCl is in error. Similarly Table 18a shows the limiting ionic conductance of Li^+ as found from Savedoff's¹⁴ lithium halides varies from 72 to 91, the value of 91 being obtained from her $\Lambda_0 = 214 \pm 4$ for LiCl . Her value of Λ_0 for LiCl appears too high, and that found in this work, namely $\Lambda_0 = 202.1 \pm 0.3$ gives $\lambda_{\text{Li}^+}^0 = 79$ which is more consistent with the other values (Table 18a).

a
TABLE 18a ...

TABLE 18a.

LIMITING IONIC CONDUCTANCES IN ACETONE AT 25°.

Ion	Electrolyte	λ , cm ² ohm ⁻¹ equiv. ⁻¹	Reference
H ⁺	HClO ₄	101	t.w.
Li ⁺	LiClO ₄ , LiClO ₄ , LiCl, LiCl ₄ , LiBr ₄ , LiI	76, 77, 79, 91, 72, 74	11, t.w., t.w., 14, 14, 14.
Na ⁺	NaClO ₄ , NaClO ₄ , NaPic	78, 86, 74	11, t.w., 8
K ⁺	KCNS, KCNS	75.7, 75.7	8, 111
NH ₄ ⁺	NH ₄ ClO ₄ , NH ₄ I	116, 103	t.w., 15
Me ₄ N ⁺	Me ₄ NPic	93	4
n-Et ₄ N ⁺	Et ₄ NPic	86	8
n-Pr ₄ N ⁺	Pr ₄ NI	70	4
n-Bu ₄ N ⁺	Bu ₄ NCLO ₄ , Bu ₄ NI, Bu ₄ NPic.	69, 58, 62	8, 8, 8
n-Am ₄ N ⁺	Am ₄ NBr	53	10
F ⁻	(CH ₃) ₄ NF	90	8
Cl ⁻	Bu ₄ NCl, LiCl, Bu ₄ NCl	125, 124, 109	14, T.W., 8
Br ⁻	Bu ₄ NBr	122	8
I ⁻	KI, KI, KI	121, 120, 116	3, 14, 8
picrate ⁻	KPic	90	8
ClO ₄ ⁻	KClO ₄ , KClO ₄	112, 113	11, t.w.
NO ₃ ⁻	Bu ₄ NNO ₃	125	4
CNS ⁻	KCNS, KCNS	125.9, 125.9	8, 111
(p-toluene) sulphonate ⁻	Bu ₄ Np-toluene sulphonate	89	14

t.w. = this work,

Pic = picrate

TABLE 18b.

PROPOSED LIMITING IONIC CONDUCTANCES IN ACETONE AT 25° C.

Ion	λ^0 , cm ² ohm ⁻¹ equiv. ⁻¹	Ion	λ^0 , cm ² ohm ⁻¹ equiv. ⁻¹
H ⁺	101	F ⁻	90
Li ⁺	78	Cl ⁻	124
Na ⁺	80	Br ⁻	122
K ⁺	75.7	I ⁻	121
NH ₄ ⁺	110	Pic ⁻	90
Me ₄ N ⁺	93	ClO ₄ ⁻	113
n-Et ₄ N ⁺	86	CNS ⁻	125.9
n-Pr ₄ N ⁺	70	NO ₃ ⁻	125
n-Bu ₄ N ⁺	62	(p-toluene) ⁻	89
n-Am ₄ N ⁺	53	(sulphonate)	

Table 18b gives proposed limiting ionic conductances in acetone at 25°. These values are the weighted average of those given in Table 18a, additional weight being given to more precise results or where the quality of the acetone used was highest. For example, the value of $\lambda_{I^-}^0$ calculated from Λ_0 of KI is 121 as found from Dippy and Hughes,³ extensive measurements on this salt in acetone. The Λ_0 data of Kraus⁸ and Savedoff¹⁴ are ignored.

A comparison of limiting ionic conductances as found here

(Table 18b) and those approximate ones calculated from Fowler's rule is given below:

Ion	Table 18b	Fowler and Kraus ¹¹⁰
Bu_4N^+	62	67
K^+	75.7	81

As might be expected (see III.6) from the discussion of ion solvation in this section and IV. 6.2 the agreement is unsatisfactory, and as all conductances in acetone will be based on the λ_o value for Bu_4N^+ ion, the results will all disagree.

The conductances of the tetrasubstituted ammonium ions decrease (Table 18b) from Me_4N^+ to $n\text{-Am}_4\text{N}^+$ as might be expected. The conductance of anions is in general considerably higher than that of comparable positive ions. For example, the conductance of the perchlorate ion is 113 while that of the Me_4N^+ ion is 93. Although the conductance of the fluoride ion (90) is relatively low, it is considerably greater than that of the potassium ion (76). The high conductance of the thiocyanate (125.9), nitrate (125) and chloride (124) ions is noteworthy. The generally high conductance of the anions implies that interaction of cations with acetone is generally greater than that of anions. Finally

the mobility of the hydrogen ion 101 is seen to be not anomalous, as it is in water.

In order to obtain further insight into the nature of ions and ion pairs and related conductance topics in acetone solution, comparisons of ion sizes will be made for certain ions concerned in this work plus F^- , Br^- and I^- ions for comparison.

The contact distance of the ions in the ion pair in acetone, a , may be estimated by means of the Denison - Ramsey⁶⁵ simplification of the Bjerrum treatment which gives:

$$-\ln K_D = \frac{1}{a \epsilon_r k T}$$

where K_D is the experimental value of the dissociation constant for the ion pair as it exists in acetone solution and k is Boltzmann's constant, the other symbols having their usual meaning. The ionic radii, r_s , in solution can be calculated using Stokes' law,¹¹³ which is approximately correct if the conditions for Stokes' law motion are satisfied.

The Stokes equation is:

$$r_s = \frac{F^2}{6 \pi N \lambda \eta}$$

where F is the Faraday and N is Avogadro's number.

$$\text{i.e. } r_s (\text{\AA}) = \frac{269.7}{\lambda} \quad \text{in acetone.}$$

The crystal radii, r_c , are from Pauling¹⁰¹ except that for the perchlorate ion which is from Hassel and Kringstad.⁹⁹

The data are shown in Table 19.

TABLE 19.

IONIC RADII AND ION PAIR SEPARATIONS.

(a, r_s and r_c in Å)

Ion	$r_c^{+,-}$	$r_s^{+,-}$	Ion pair	$r_c^+ + r_c^-$	$r_s^+ + r_s^-$	a
Li ⁺	0.60	3.44	LiClO ₄	3.00	5.82	3.71
Na ⁺	0.95	3.37	NaClO ₄	3.35	5.75	4.27
K ⁺	1.33	3.56	KClO ₄	3.73	5.94	4.78
NH ₄ ⁺	1.48	2.45	NH ₄ ClO ₄	3.88	4.83	5.56
F ⁻	1.36	2.98	LiCl	2.41	5.62	2.15
Cl ⁻	1.81	2.18	KCNS	-	5.70	4.92
Br ⁻	1.95	2.21	KPic	-	6.55	4.82
I ⁻	2.16	2.23				
ClO ₄ ⁻	2.40	2.38				
Picrate ⁻	-	2.99				
CNS ⁻	-	2.14				

The crystal radii for the halide ions are seen to increase from F⁻ to I⁻, as do the Stokes radii except for F⁻. The values of r_c^- and r_s^- are in reasonably good agreement for Cl⁻, Br⁻ and I⁻ which suggests that solvation of these

halide ions does not occur to any great extent, if at all, in acetone, and the same may be said for the ClO_4^- ion. For the latter ion the crystallographic radius (2.40 Å) and Stokes radius (2.38 Å) are in excellent, if somewhat fortuitous, agreement.

However, for the cations the Stokes radii are without exception considerably larger than the crystal radii, which probably means that considerable solvation of these cations has occurred. Although the conditions for the validity of Stokes law are not completely fulfilled for very small ions, it can be concluded that solvation of some cations is greater than that of some anions in acetone solution as in other dipolar aprotic solvents⁶¹ (see III. 6). Deductions using Stokes' law in this form have been made by many workers^{9,10,3} and introduction of the 'corrected' stokes radii¹⁰ is not necessary for the purposes of this discussion (since the same conclusions will be obtained.) The stronger solvation of many cations compared to most anions in acetone is perhaps understandable when one considers the acetone dipole. The partially positive carbon of the dipole is somewhat shielded by two methyl groups and the positive charge will also be partly distributed over these groups, while the negative end is unshielded.

The conductance data of Kraus and co-workers^{4,8} combined with this transference work, lead to the radius for the fluoride ion shown ($r_s = 2.98$) and Pauling's r_c is 1.36 Å. This ion is the exception to any generalization regarding the lack of anion

solvation in acetone. The r_o value is much smaller than the r_s value, suggesting considerable solvation in acetone. It may be possible that below some certain critical r_o value solvation occurs to a greater extent, since the bare F^- ion is notably smaller than the other halide ions. (r_o values).

The ion pair contact distances, a , are all larger than the sum of the crystal radii, $r_o^+ + r_o^-$, except for LiCl. This suggests that the cations, or possibly the anions to a lesser extent, or both ions retain a firmly held solvation sheath in the ion pair. The a value, deduced from conductance theory, for LiCl (2.15Å), is clearly impossible when the sum of the crystallographic radii (2.41Å) is considered. Similar impossibilities have been found by Kay⁶⁷ for certain alkali halides in various solvents, and it may be some fault of the model used as the basis for the conductance theory. It seems likely that in LiCl the unsolvated ions are in contact in the ion pair in acetone.

The sum of the Stokes radii, $r_s^+ + r_s^-$, is generally larger than the corresponding ion pair radius, a , except for ammonium perchlorate (Reynolds and Kraus⁸ conductance data were used for KCNS and KPic). This suggests that some mutual penetration of the anion and cation solvation sheaths occurs when the ion-pairs form, which is not unreasonable. In view of the previous discussion this would probably be primarily anion penetration of the cation solvation sheath. The generally larger Stokes radii compared to the

ion pair contact distance in solution can be deduced for many similar salts (including these four perchlorates) in methanol^{67,115} and in water⁶⁷ to a lesser extent. The situation as regards ammonium perchlorate, where the Stokes radii sum (4.83\AA) is less than the ion pair separation (5.56\AA), is interesting. A possible explanation is that the solvation sheath in the ion pair is not retained when the ions move through the solvent. Comparison of $r_c^- = 2.40\text{\AA}$ and $r_s^- = 2.38\text{\AA}$ for the perchlorate ion suggests that it would be primarily, if not solely, the ion sheath of the ammonium cation that is lost, which is not unreasonable considering the relatively large size of the NH_4^+ ion (1.48), which is the biggest cation studied, and consequent low charge density in the ion. Gordon and co-workers²⁴ have stated that solvation cannot be treated as a purely electrostatic problem in many cases, but that other types of ion-solvent interaction are involved as well. It appears that some such interaction between ammonium ion and acetone molecule(s) is important.

Of those solvents for which precise transport numbers have been determined, acetone has the lowest relative permittivity ($\epsilon_r = 20.47$). Limiting ionic conductances can be used to provide a precise test of the constancy of the Walden⁵ $\lambda_o\eta$ product for ions over a large range of relative permittivities and viscosities from $\epsilon_r = 20.47$ and $\eta = 3.04$ mpoise in acetone to $\epsilon_r = 109.5$ and $\eta = 33.0$ mpoise in formamide.⁸⁰ It should be noticed that η and ϵ_r increase from acetone to formamide (left to right, Table 20.).

TABLE 20.

CONDUCTANCES AND WALDEN PRODUCTS IN A RANGE OF SOLVENTS.

Solvent	$(\text{CH}_3)_2\text{CO}$	$\text{CH}_3\text{NO}_2^{91}$	H_2O^{10}	HCONH_2^{80}
$10^3\eta$	3.04	6.27	8.95	33.0
ϵ_r	20.47	36.7	78.5	109.5
Ion				
$\text{Me}_4\text{N}^+ \lambda_0$	92.9	55.0	44.9	12.5
$\lambda_0\eta$	0.28	0.34	0.40	0.41
$10^2\lambda_0\eta$	1.36	0.94	0.51	0.37
$\frac{\lambda_0\eta}{\epsilon_r}$				
$\text{Et}_4\text{N}^+ \lambda_0$	86.3	47.7	32.7	10.0
$\lambda_0\eta$	0.26	0.30	0.29	0.33
$10^2\lambda_0\eta$	1.27	0.81	0.37	0.30
$\frac{\lambda_0\eta}{\epsilon_r}$				
$\text{Cl}^- \lambda_0$	124	62.7	76.4	17.1
$\lambda_0\eta$	0.38	0.39	0.68	0.56
$10^2\lambda_0\eta$	1.85	1.07	0.87	0.51
$\frac{\lambda_0\eta}{\epsilon_r}$				
$\text{Br}^- \lambda_0$	122	62.9	78.2	17.2
$\lambda_0\eta$	0.37	0.39	0.70	0.57
$10^2\lambda_0\eta$	1.80	1.08	0.89	0.52
$\frac{\lambda_0\eta}{\epsilon_r}$				

Data for such a test are given in Table 20 for four solvents at 25° C. Four ions will be considered: Me_4N^+ , Et_4N^+ , Cl^- and Br^- . The relative permittivity is taken into account with the function

$$\lambda_0 \eta / \epsilon_r \quad \text{suggested by Van Rysselberghe and Fristrom.}^{115}$$

Some interesting relationships are apparent. The conductance of the cations is seen to decrease from left to right, but the anions exhibit sudden conductance increase for water. As in many of its properties, water shows a marked anomaly in this respect.

The supposedly constant Walden product, which can be derived from Stokes' law, is seen to be more constant for cations than the anions, where it varies for water and formamide, which are of high relative permittivity. However, Van Rysselberghe and Fristrom's function with its correction for relative permittivity is no more successful, and it seems that the effect of variation of dielectric constant does not appear to be easily interpreted. The fact that the Walden product is constant for the anions in acetone and nitromethane may mean that the degree of solvation, if any, in these two solvents is similar.

However, for these four solvents, which cover the widest range of dielectric constant and viscosity over which such comparisons have yet been made, the Walden and Van Rysselberghe - Fristrom rules fail. This merely emphasizes the need for additional transference work in non-aqueous solvents. The eventual

correlation of ionic mobility with ion and solvent properties will be in terms of specific ion-solvent and ion-pair interaction. At present it seems that complete explanation of ionic mobility as a function of solvent properties is not possible, and a different approach to this problem in terms of transition state theory has recently been suggested.¹¹⁶

PART V.DIFFUSION OF HYDROGEN CHLORIDE IN ACETONEAT THREE TEMPERATURES.V. 1 Introduction.

The conductance of hydrogen chloride in acetone has been determined by Sackur,¹ Mackor and Spaarnay,² Ross Kane,⁹ Hotz,¹⁶ Sadie¹³ and Everett and Rasmussen¹¹⁸ at 25° and by Dorofeeva and Kudra²⁷ from -21.2° to 0° C. All these workers, except for Sackur, whose results were incorrect, came to the conclusion that complexing of some sort occurs in the hydrogen chloride acetone system. In a review of the conductances of hydrogen halides in organic solvents, Janz and Danyluk¹²⁹ came to similar conclusions. They mention complexes of the type $[(CH_3)_2CO]_x - (HCl)_y$ where $x = 1$ or 2 and $y = 1, 3$ or 5 . Braude³⁰ has shown the existence of $(CH_3)_2COH^+$ in such solutions and Mackor²⁸ was of the opinion that HCl dimerised in acetone solutions. Hotz¹⁶ suggested that aggregates containing up to twelve hydrogen chloride molecules might exist in equilibrium with smaller such complexes.

In general it was found that reproducible conductance and e.m.f. measurements were very difficult to obtain^{2, 29} particularly at 25°. None of the above workers was able to obtain a precise limiting equivalent conductance for hydrogen chloride solutions in acetone, the position being further complicated by the fact that

such solutions tend to be unstable. The instability of these solutions can be ascribed to an acid catalysed self-condensation of acetone. Dorofeeva and Kudra²⁷ suggested the existence of a 'compound' of hydrogen chloride and acetone similar to that of pyridine and HCl, pyridine hydrochloride. Even with conductance measurements at very low concentrations conventional Fuoss plots have not been straight lines, but show marked changes of slope.^{13,16} One conclusion can be obtained from this work,^{9,13,16} namely, that hydrogen chloride is a very weak acid in acetone with a dissociation constant of the order of 10^{-7} . This weakness, combined with the instability of the HCl-acetone system and the formation of ill-defined complexes, renders it not too surprising that conductance measurements have failed to produce conclusive results other than that the acid is very weak in acetone solutions.

In an attempt to throw some light on the HCl-acetone system, Sadie¹³ measured diffusion coefficients at 25° and obtained a curve of D against $C^{\frac{1}{2}}$ with a minimum at about 0.04M HCl concentration, which is, however, very doubtful as the 'duplicate' value of D for this concentration was very high¹³¹ and would have resulted in a maximum at this concentration. In addition the agreement of other duplicate determinations was very poor, and a possible reason for this will be suggested in (V. 4.2). In an effort to add to existing knowledge, it was decided to measure diffusion coefficients of hydrogen chloride in acetone at 15°, 25° and 35° as a function of concentration.

V. 2 Choice of Method.

There are several methods commonly used for measurement of diffusion coefficients in solutions. Chief among these are the porous diaphragm technique,¹³² the isotopic tracer capillary tube method,¹³³ the conductimetric method¹³⁴ and various optical methods, such as the Lamm transparent scale method¹³⁵ and Goüy interference method.¹³⁵ The diaphragm cell method gives relative results and cannot be used below 0.05 M due to surface diffusion over the large area of glass provided by the sinter. The conductimetric method requires several days for a single measurement and hydrogen chloride solutions in acetone are unstable with respect to time. Optical methods are also unsuitable at low concentrations where the change in refractive index would be very small. The isotopic tracer technique of Anderson and Saddington¹³³ was therefore adopted.

This method involves use of a uniform capillary tube of known length, filled with a solution in acetone of isotopically normal carrier HCl and tracer $H^{36}Cl$. The tube is immersed in a large vessel containing an inactive solution of the same concentration, and these inactive solutions are very gently stirred with a small magnetic stirrer. The activity of the solution in the capillaries is measured before and after diffusion, thus enabling calculation of the diffusion coefficient. The inactive solution is stirred to ensure that the concentration of active isotope at the mouth of the capillary tube is zero (see V. 5.1). The active and

inactive solutions must be of the same total hydrogen chloride concentration to ensure that mass diffusion of hydrogen chloride is eliminated.

V. 3 Apparatus and Solutions.

3.1 The Diffusion Cell and Capillary Tubes.

Three similar sets of apparatus were made for use at the three temperatures 15° , 25° and 35° . One set will be briefly described, the design being similar to that of Sadie¹³ which incorporated suggestions of Davies.¹³⁸

The cell design and tubes are shown in figure 29. The capillary diffusion tubes were constructed according to the method of Davies¹³⁸ who recommended tubes of about 0.5 mm internal diameter, about 2 cm. in length and with the open ends tapered to 30° cones. Tubes of greater diameter cause losses of active material due to a scooping out of this material by inactive solution sweeping across the top of the tube. Longer tubes require an inconveniently long diffusion time, since the ratio of the activity after diffusion to that before diffusion should be not greater than 0.5 for accurate results.¹³⁸ About a dozen tubes were made, and six with a flat inner base were selected after rotation under a microscope and filling with mercury to show up irregularities. The open ends were tapered so as to reduce the sweep of inactive solution across the top of the tubes. The internal length of each capillary tube was measured 10 times on a travelling microscope, and the mean lengths are recorded in Table 21.

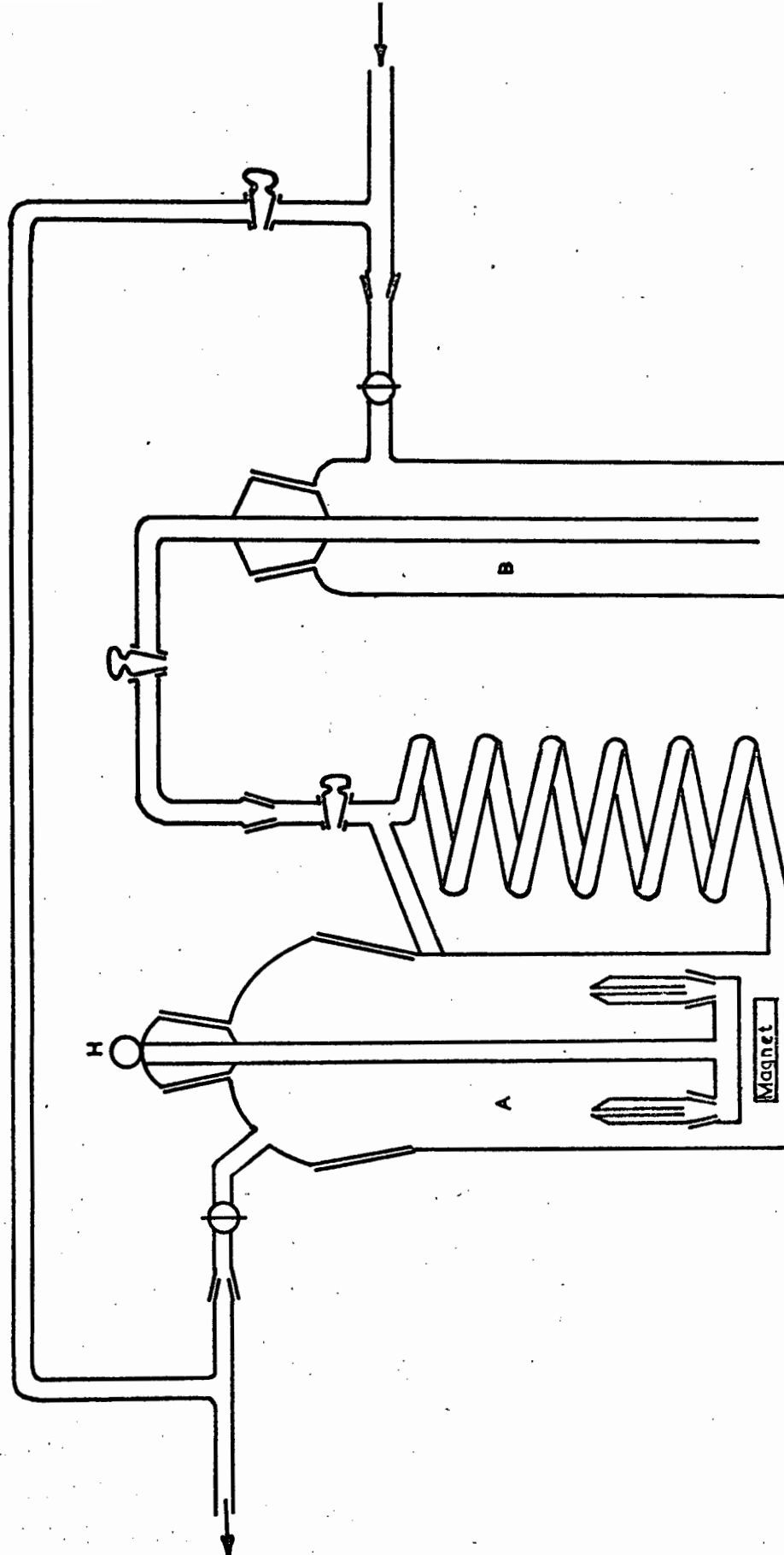


Fig. 29. A diffusion cell.

TABLE 21.INTERNAL LENGTH OF CAPILLARY DIFFUSION TUBES.

Tube number	1	2	3	4	5	6
Length, cm.	2.1720	2.2061	1.9668	2.0112	1.7729	2.3476
Standard Deviation, cm.	0.0004	0.0005	0.0004	0.0005	0.0003	0.0006

The cell (fig. 29) is seen to consist of a rotatable tube holder mounted in a ground glass joint in a container for the solutions in which the tubes will be immersed. The inactive solution was stored in container B, and could be blown over into the diffusion chamber, A, with dry nitrogen, through the coil shown. The spiral coil¹³⁸ served to help in bringing the entering liquid to the equilibrium temperature. The essential difference between this apparatus and that of Sadie¹³ is the provision made for stirring with a small magnet.

3.2 Preparation, Storage and Analysis of Hydrogen Chloride Solutions in Acetone.

All apparatus was thoroughly cleaned in a sulphuric acid - nitric acid cleaning mixture. Solutions of inactive hydrogen chloride in anhydrous acetone were prepared by bubbling the gas through the liquid for about twenty minutes. The pure gas was

generated by the action of concentrated sulphuric acid on concentrated hydrochloric acid, and dried by passing through concentrated sulphuric acid and over anhydrous magnesium perchlorate. It was then passed into a saturator containing acetone. The entire apparatus¹³ was flushed with dry nitrogen before use. The open end of the saturator was connected to a drying train and acid absorbing soda lime. Active solutions were prepared in a similar manner to the inactive solutions on a smaller (quarter) scale and using 3 ml of $H^{36}Cl$ containing about 240 μc and 3 ml of concentrated carrier HCl . These proportions were found to be the most suitable from trial experiments. Details of the gas generating apparatus have been described by Sadie,¹³ the procedure used being that described here.

Dilutions of the stock solutions of hydrogen chloride in acetone were prepared by weight and stored in sealed tubes at -80° in a deep freeze in a dry ice and acetone cooling mixture.

Relatively large (25 ml) quantities of active solution were necessarily prepared, and only very small volumes (< 0.2 ml) were used for each pair of duplicate determinations, allowing for wastage in the syringe used for filling the tubes. (V. 4.1). Hence the active solution was divided into three, and each third stored in a separate small sealed tube, which was immersed in dry ice and acetone. The first third was used in preparing the two most concentrated solutions, the next for two more dilute solutions

and the final fraction for the three most dilute solutions. All seven concentrations were studied at three temperatures.

Storage at -80° was shown by Sadie¹³ to prevent self-condensation in these solutions for at least 9 days for a 0.65 M solution. A test, by ultraviolet spectroscopy at 2310 Å, for the presence of mesityl oxide in the active solution kept for the longest period at -80° , namely, the 0.00412 M solution after 20 days, showed no mesityl oxide. All inactive solutions were prepared not more than seven days before use, and diffusions were carried out with the most concentrated solutions first. More than one batch of active solution per series of experiments was not prepared in view of the high cost of H^{36}Cl .

The solutions were analysed volumetrically by titration with standard caustic soda. The sodium hydroxide was stored in a polythene container connected to a carbon dioxide free apparatus permanently fitted to a self-balancing burette fitted with a side arm. This enabled titrations to be performed out of contact with the atmosphere, any openings to the atmosphere being via guard tubes of soda lime. The sodium hydroxide was periodically standardised against potassium hydrogen phthalate, and its concentration changed by less than 0.0003 moles/litre during the entire course of this section of the work.

Triplicate determinations of the hydrogen chloride concentration, which were performed by addition of 70 ml of freshly boiled

distilled water to a weighed sample of the hydrogen chloride solution and titrating with the standard alkali using screened methyl orange indicator, were found to agree within 2×10^{-4} moles/litre.

V. 4 Experimental Procedure.

4.1 The Diffusion Procedure.

All manipulations of acetone solutions were performed in an atmosphere of dry nitrogen in a dry box.

The capillary tubes were carefully filled with a hypodermic syringe, care being taken to ensure that no bubbles formed in the tube. They were placed in their holders (fig. 29), the chamber, A, being partly filled with inactive solution to just below the level of the top of the capillaries. The storage chamber, B, was filled with inactive solution and the apparatus removed from the dry box.

The apparatus was then assembled in a thermostat at 15° and after thermal equilibrium was attained, the inactive solution in vessel B was forced into chamber A with dry nitrogen at a rate of about 20 ml/min. The time when the liquid in A just covered the tips of the capillary tubes was noted, time being measured with a stop-watch and chronometer. The inactive solution covered the active solution in the two tubes to a depth of 2 cm above the top of the tubes. The solution was gently stirred by means of handle H (fig. 29) and the small magnet.

Two diffusion cells were filled and set up in water baths controlled at $25.00^{\circ} \pm 0.01^{\circ}$ and $35.00^{\circ} \pm 0.01^{\circ}$ by Braun Thermomix II thermostats. A third cell was set up in a water bath containing copper cooling coils, through which chilled water at 10° was pumped by a Buhler Superthermostat. The water bath was held at $15.00^{\circ} \pm 0.02^{\circ}$ by a Braun Thermomix II. All thermostats were mounted on vibration absorbing sponge rubber mats.

Diffusion was allowed to proceed for about $10\frac{1}{2}$ hours at 15° , 10 hours at 25° and $9\frac{1}{2}$ hours at 35° , which gave $\gamma = \frac{c_{av}}{c_o}$ values of between 0.22 and 0.46.

On completion of diffusion the liquid was blown back into B, the time of appearance of the capillary tube tips above the surface of the solution being noted, using a stop-watch in conjunction with a chronometer.

4.2 Determination of the Activities.

An initial trial 'run' was performed at 25° . The two capillary tubes, which enable duplicate results to be obtained at each concentration, were carefully washed out with distilled water, using a hypodermic syringe, and counted in a stoppered Geiger-Muller liquid counter with a superimposed paralysis time of 500μ sec. The efficiency of washing was determined by collecting further washings and comparing the activity of these washings with the background count obtained with distilled water.

The above counting procedure using a Geiger-Muller tube was that employed by Sadie,¹³¹ who also washed his active solutions of acetone into a liquid counter using water. The results found in this trial run had an enormous scatter, almost as great as that found by Sadie.¹³ The probable reason for this is that even the highest concentration of acid used only resulted in counts of less than twice the background (ca. 18 c.p.m.), with a consequently large statistical error. Higher concentrations of active H^{36}Cl could not conveniently be used as the radioactive isotope solution is expensive.

Chlorine-36 is a moderately soft β emitter and it was decided to attempt counting this isotope by a liquid scintillation procedure. Although it was thought that acetone would act as a strong scintillation quencher, the small quantity of acetone present, (ca. 0.02 ml) in about 10 ml of scintillator solution, suggested that the method was worth trying, and indeed it eventually proved successful. The final procedure adopted is described below.

The liquid scintillation mixture^{137,128} was prepared as follows: 3.0g of 2,5-diphenyloxazole and 0.3g of 1,4-bis(2-(5-phenyloxazolyl))-benzene, both scintillation grade as supplied by the Packard Instrument Company, were dissolved in one litre of redistilled Judex Analar toluene. The contents of the capillary tubes containing active solution were flushed directly into Packard Scintillation bottles with 10 ml of this scintillation solution.

This direct procedure avoids some of the sources of error in the G-M counting method where active solution was flushed into 10 ml volumetric flasks and had to be subsequently transferred to a liquid counter. The efficiency of washing was verified by collecting further washings and showing that the counts given by these did not differ significantly from the background count.

The most efficient counting procedure eventually found was one whereby solutions were chilled to about -4°C and counted at this temperature. This was achieved using a "Packard Tri-Carb Model 314 - EX" scintillation counter. All solutions were counted to at least 30,000 counts, giving a counting precision of better than 0.6%. The background count at -4° was about 18 c.p.m. as found using a blank consisting of a capillary of inactive solution flushed into a counting bottle with 10 ml of scintillation solution.

In order to determine the initial activity before diffusion, the procedure described in V. 4.1 was followed up to the stage where temperature equilibrium of the solutions in vessel A had been attained. At this stage the tubes were flushed out with scintillation solution.

The results of the trial run at 25° using distilled water and a Geiger counter were discarded. Three separate series of experiments were performed at each of the three temperatures used, giving a total of six results for each concentration at each

temperature. The four results at each concentration from the first two series of experiments agreed satisfactorily, but a third series was nevertheless performed since the diffusion curves obtained were thought to be most unusual. (See V. 5.2) The third series confirmed the original results within experimental error. The experiments were performed starting with the most concentrated solution, which would be most liable to self-condensation in the presence of HCl, and finishing with the most dilute solution.

V. 5 Results and Discussion.

5.1 Calculation of Results.

Diffusion is often a process which leads to an equalization of concentration within a single phase. The laws of diffusion connect the rate of flow of the diffusing substance with the concentration gradient responsible for this flow. If the diffusion coefficient, D , is constant for a given experiment then the equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \dots 5.1.1$$

which is often called Fick's second law of diffusion, may be derived.¹³⁵

For the conditions of these experiments equation (5.1.1) may be solved as follows:¹⁰

$\frac{\partial c}{\partial x}$ is the rate of increase of concentration, c , with distance, x , measured in the direction of flow;

and $\frac{\partial c}{\partial t}$ is rate of concentration increase with respect to time, t .

If it is assumed that c can be expressed as a product of separate functions of x and t only

$$c = F(x) \cdot f(t)$$

$$\text{then } \frac{\partial c}{\partial t} = F(x) \frac{d}{dt} f(t)$$

$$\text{and } \frac{\partial^2 c}{\partial x^2} = f(t) \frac{d^2}{dx^2} F(x)$$

Hence (5. 1.1) becomes

$$\frac{1}{Df(t)} \cdot \frac{d}{dt} f(t) = \frac{1}{F(x)} \frac{d^2}{dx^2} F(x) \quad \dots 5. 1.2$$

Since the left and right hand sides of this equation are functions of t only and x only respectively, the equation can be satisfied only if each side is separately equal to the same constant, $-k^2$.

$$\text{Hence } \frac{d}{dt} f(t) = -k^2 Df(t) \quad \dots 5. 1.3$$

$$\text{and } \frac{d^2}{dx^2} F(x) = -k^2 F(x) \quad \dots 5. 1.4$$

A physically permissible solution is

$$c = b \exp (-k^2 Dt) \cdot F(x)$$

where $F(x)$ is a solution of (5. 1.4) and b is a constant. In the capillary tube method, the boundary conditions for a tube closed at $x = 0$ and open at $x = a$, where a is the length of a tube, are:

$$\text{At } t = 0, c = c_0 \text{ for } 0 < x < a, \quad c = 0 \text{ for } x > a$$

At $t > 0$, $c = 0$ at $x = a$ and $\frac{\partial c}{\partial x} = 0$ at $x = 0$

These conditions can be satisfied only if

$$k = \frac{2n+1}{2a} \pi \quad \text{where} \quad n = 0, 1, 2, \dots$$

since $F(x)$ from equation 5.1.4 must be a sine or cosine function. The solution is:

$$c = \sum_{n=0}^{\infty} B_n \exp \left[-\pi^2 (2n+1)^2 Dt / (4a^2) \right] \cos \frac{\pi(2n+1)x}{2a}$$

By Fourier analysis, it is found that the coefficients, B_n , are given by

$$B_n = (-1)^n \frac{4c_0}{\pi(2n+1)}$$

and hence

$$\frac{c}{c_0} = \sum_{n=0}^{\infty} (-1)^n \frac{4}{\pi(2n+1)} \exp \left(-\pi^2 (2n+1)^2 Dt / (4a^2) \right) \cdot \cos \frac{\pi(2n+1)x}{2a}$$

The average concentration in a tube at time t is

$$c_{av} = \frac{1}{a} \int_0^a c \, dx$$

whence

$$\frac{c_{av}}{c_0} = \sum_{n=0}^{\infty} \frac{8}{\pi^2 (2n+1)^2} \cdot e^{-\pi^2 (2n+1)^2 Dt / 4a^2} \quad \dots 5.1.5$$

Equation 5.15 can be rewritten in the form

$$\frac{c_{av}}{c_0} = \gamma = \frac{8}{\pi^2} \left(\frac{e^{-\theta}}{1} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \frac{e^{-49\theta}}{49} + \dots \right)$$

$$\text{where } \theta = \pi^2 Dt / 4a^2$$

$$\therefore \gamma = \frac{8}{\pi^2} e^{-\theta} \left(1 + \frac{e^{-8\theta}}{9} + \frac{e^{-24\theta}}{25} + \dots \right)$$

$$\text{i.e.} \quad \gamma = \frac{8}{\pi^2} e^{-\theta} \cdot F \quad \dots 5.1.6$$

Hence

$$\log \gamma = \log \frac{8}{\pi^2} - \frac{\pi^2 Dt}{4a^2} \log e + \log F$$

$$\text{and} \therefore D = \frac{4a^2}{\pi^2 t \log e} \left(\left(\log \frac{8}{\pi^2} - \log \gamma + \log F \right) \right) \quad \dots 5.1.7$$

For a given tube, concentration and temperature, D and a are constant, the only variable in θ being t . For selected values of θ corresponding values of F could be calculated according to equation (5.1.6), which embodies the definition of F . For these values of F corresponding values of γ could be calculated from equation 5.1.6 and the data (Table 22) used to construct a plot of F against γ (Fig. 30).

TABLE 22...

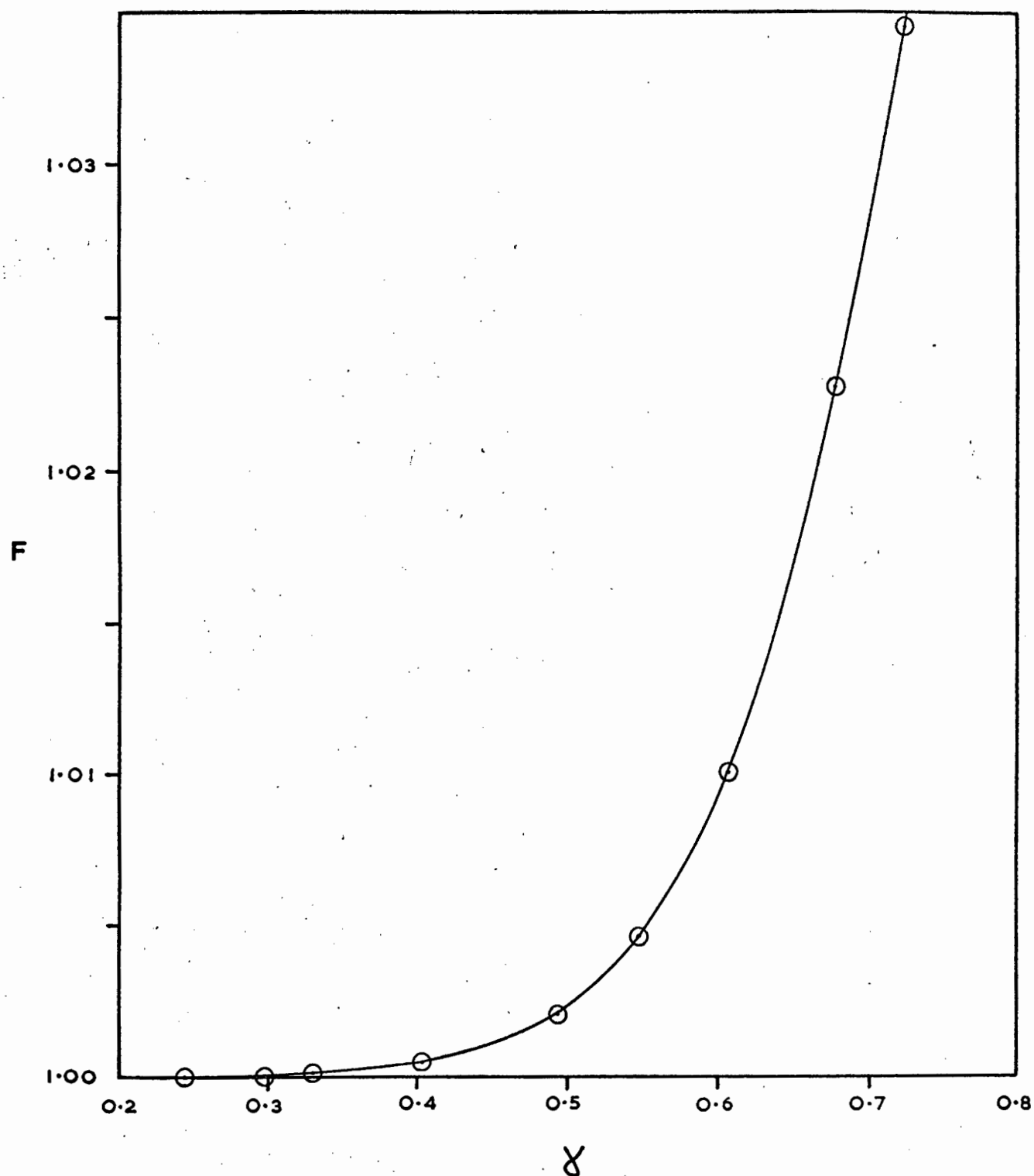


Fig. 30. Plot of F against γ for use in the calculation of diffusion coefficients.

TABLE 22. θ , F AND γ VALUES FOR CALCULATION OF D.

θ	F	γ
0.15	1.03455	0.7236
0.20	1.02275	0.6789
0.30	1.01011	0.6067
0.40	1.00453	0.5459
0.50	1.00200	0.4927
0.70	1.00041	0.4028
0.90	1.00008	0.3299
1.00	1.00004	0.2983
1.20	1.00000	0.2443

From this plot values of F could be read off for the experimental values of $\gamma = \frac{c_{av}}{c_o}$ and

thus equation (5. 1.7) could be solved for the diffusion coefficient, D. Figure 30 is a small scale copy of the plot actually used.

The results are shown in Table 23.

TABLE 23...

TABLE 23.

DIFFUSION COEFFICIENTS OF HYDROGEN CHLORIDE IN ANHYDROUS ACETONE

Hydrogen Chloride Concentration mole litre ⁻¹				Diffusion Coefficients							
Active Solutions, c	Inactive Solutions			C ^{1/2} mole ^{1/2} litre ^{-1/2}	No. of results used			10 ⁵ D cm ² sec ⁻¹			
	15°	25°	35°		15°	25°	35°				
0.10023	0.1001	0.10084	0.1000	0.3194	6	6	6	4.99±0.08	3.47±0.05	4.24±0.07	
0.05678	0.0562	0.05644	0.0569	0.2383	6	6	5	3.64±0.06	2.76±0.05	4.14±0.07	
0.04611	0.0467	0.04557	0.0463	0.2147	5	6	6	4.35±0.07	3.22±0.05	4.86±0.08	
0.03399	0.0341	0.03427	0.0337	0.1843	6	6	5	5.27±0.09	3.81±0.07	5.07±0.09	
0.02596	0.0256	0.02653	0.0259	0.1611	6	6	5	3.32±0.06	2.97±0.05	3.87±0.07	
0.01883	0.0181	0.01893	0.0185	0.1372	6	6	6	1.80±0.04	2.71±0.05	2.89±0.05	
0.00412	0.0042	0.00419	0.0041	0.0642	6	6	6	3.08±0.09	4.06±0.12	4.49±0.12	

Five values of D were averaged in the four cases shown since the sixth value differed from the mean of the rest by more than three times the standard deviations quoted.

The density of acetone at 25° was taken as 0.7844.⁸ The density at 15° was taken as 0.7957 and that at 35° was obtained from a curve drawn for density data from 20° to 50° , all these values being taken from Timmermans.⁹⁶ The density of the solutions was assumed equal to that of the solvent, which is satisfactory for these calculations. Hence the concentrations, which were measured at about 25° , could be calculated at the relevant temperatures for active and inactive solutions. For purposes of comparison, plots of D against C were made for results at 15° and 35° and the diffusion coefficients at the active concentrations shown in Table 23 were read off.

The standard deviations shown in Table 23 are similar to those usually obtained with this capillary tube method.^{10,143}

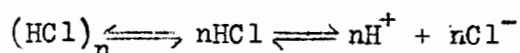
5.2 Discussion of Results.

The diffusion of pure anhydrous hydrogen chloride in anhydrous acetone is diffusion of an extremely weak electrolyte with a dissociation constant of about 10^{-7} (V.1). Also, as mentioned in V.1, the conductance results of various workers suggest some form of complexing in these solutions.

A survey of the literature shows that very few diffusion coefficients of weak electrolytes have been measured, even in aqueous solution. In diffusion of dissociated electrolytes, both ions must move in the same direction at the same speed, since it has been found that no charge separation occurs. In dilute solutions

the motion of the solvent can be ignored and the diffusion coefficient can be regarded as describing the motion of the solute particles through a stationary solvent.

When the low K_D for hydrogen chloride in acetone is considered, it is clear that most of the solute diffuses in the form of molecules or other undissociated forms. No attempt will be made, at this stage, to suggest what the diffusing particles are in the acetone - HCl system. The "force" producing diffusion can, in general, be considered as being the gradient of the chemical potential in the solution.¹³⁹ Assuming the equilibria



the chemical potential of the HCl unit is the same in all forms whether solvated or not, since they exist in equilibrium and the free energy gradient of the solute is therefore the same for all forms.

One way in which ion association affects the diffusion coefficient concerns the fact that when two particles merge into one they experience less resistance to motion through the liquid, which increases the diffusion coefficient.¹⁰ The laws governing the motion of simple associated electrolytes have been derived by Harned and Hudson⁴⁰ and may be obtained from the equation¹³⁹

$$D = \left[\alpha (D^0 + \Delta_1 + \Delta_2) + 2(1 - \alpha) D_{12}^0 \right] \left(1 + c \frac{d \ln f_{\pm}}{dc} \right)$$

where f_{\pm}^+ is the mean molar activity coefficient and Δ_1 and Δ_2 are first and second order electrophoretic terms and D_{12}^0 represents

the hypothetical diffusion coefficient of an ion pair or molecule at infinite dilution and is defined by $D_{12}^0 = kTu_{12}$, u being the absolute mobility. If u_1 and u_2 are absolute mobilities of ions 1 and 2 and α the degree of dissociation, then equation (5. 2.1) can be written¹⁴⁴

$$D = 2 kt \left(1 + c \frac{d \ln f_{\pm}}{dc} \right) \left[\alpha \frac{u_1 u_2}{u_1 + u_2} + (1 - \alpha) u_{12} \right] \quad \dots 5. 2.2$$

These equations presented above and those following, are, in fact, not applicable to this case which involves tracer diffusion of a very weak electrolyte which, as will be seen later, appears to polymerise in acetone solution. In the particular situation involved in this work, radioactive hydrogen chloride molecules (and some $^{36}\text{Cl}^-$ ions) are diffusing into a large excess of inactive solution at the same concentration. The tracer diffusion coefficient of the molecule could be considered as the self-diffusion coefficient of the molecule in acetone solution. The electrophoretic effect can now be neglected since the concentration of diffusing molecules is extremely small, but the relaxation effect cannot be neglected as was done for the derivation of equation (5. 2.1). This is because the active molecule is moving relative to a background of non-diffusing molecules,¹⁰ whereas in 'ordinary' diffusion of a single electrolyte all the ions are moving with the same velocity. The complex problem of theoretically determining the relaxation effect in self-diffusion has been partly solved by application¹⁴¹ of Onsager's theory to give the following

expression for the diffusion coefficient of ionic species in univalent electrolytes

$$D_i' = D_i^0 \left[1 - \frac{2.801 \times 10^6}{(\varepsilon T)^{3/2}} (1 - (du_1)^{1/2}) c^{1/2} \right] \quad \dots 5.2.3$$

where D_i' is the diffusion coefficient of an ion i present in vanishingly small amounts in an otherwise uniform electrolyte solution. The function $(du_1)^{1/2}$ depends on the mobilities and valencies of the ions present. For univalent ions 1, 2 and 3, where species 1 is the active isotope of ion 2, and 3 is thus the ion of opposite sign to 1 or 2, du_1 is defined as

$$du_1 = \frac{\lambda_2^0 + 3\lambda_3^0}{4(\lambda_2^0 + \lambda_3^0)} = \frac{1 + 2t_3^0}{4}$$

where t_3^0 is the limiting transport number of the ion 3.

Equation (5.2.3.) thus represents the Onsager limiting law for tracer diffusion at low total ionic strengths. The limiting value of this self-diffusion (or tracer diffusion) coefficient is given by the Nernst¹⁴² expression which for this case is,

$$D_i^0 = \frac{RT\lambda_i^0}{F^2} \quad \dots 5.2.4$$

It is important to notice that equation 5.2.3 describes a limiting law, and very precise data at low concentrations are required to test it.

Plots of D against $c^{1/2}$ for the data of Table 23 are shown in Figure 31.

The curves at the three temperatures are seen to be similar in

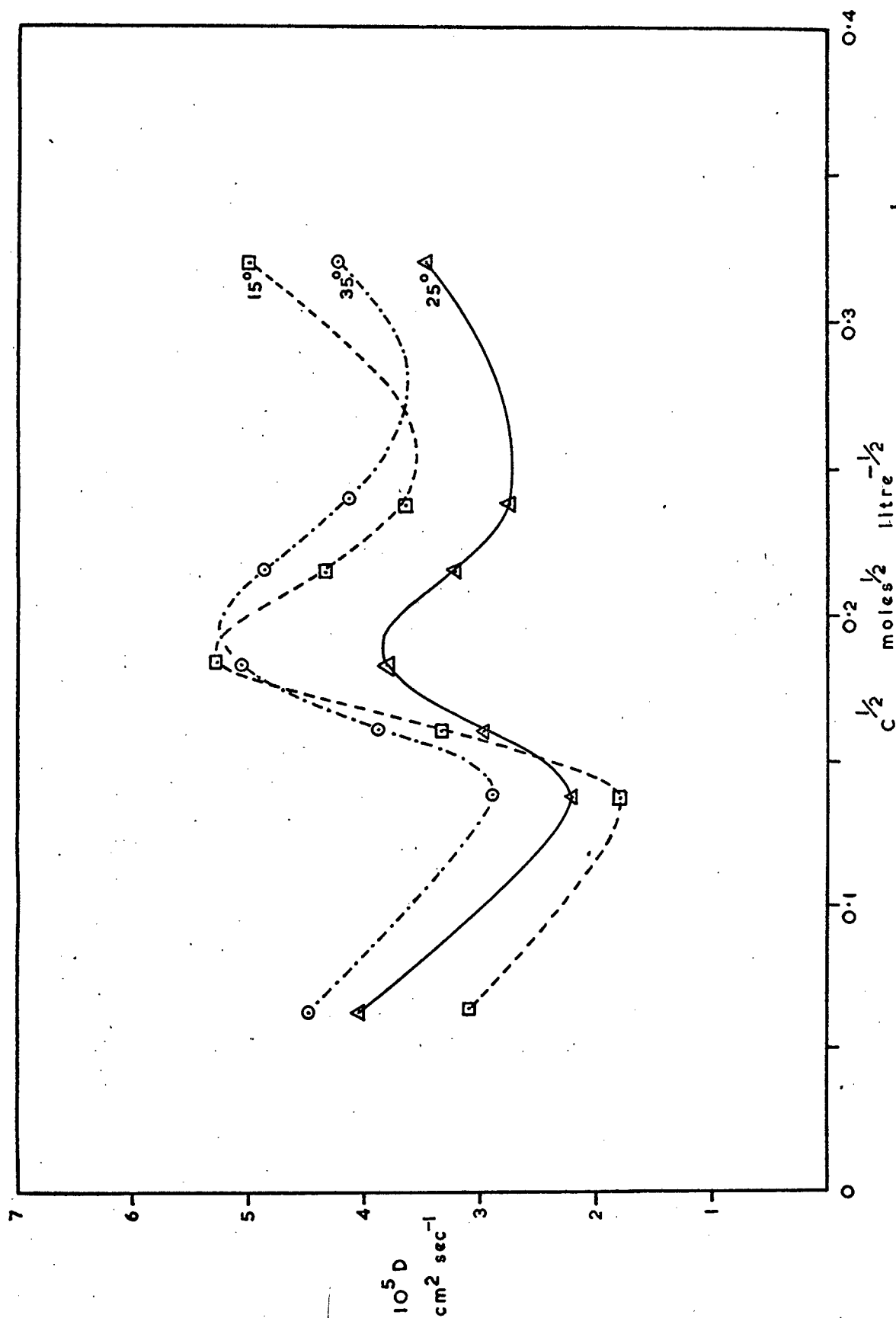


Fig. 31. Plot of diffusion coefficients against $(\text{concentration})^{1/2}$ for hydrogen chloride in acetone.

general shape, but results at 35° are not reliable because at this temperature the four most concentrated solutions showed some yellow colouration at the end of a diffusion experiment. This indicates that some deterioration of the solvent had occurred after about 10 hours at 35° in the presence of hydrogen chloride, and these results will therefore be ignored in further discussion.

Hydrogen chloride concentrations greater than about 0.12 molar could not be used as self-condensation occurred after 10 hours at 25° in this solution, as found in a trial experiment. Concentrations of about 0.1 M and less were used. The two or three lowest concentrations at 35° may be expected to give reasonably accurate diffusion coefficients as no solvent deterioration could be (qualitatively) detected. At the two lowest concentrations the diffusion coefficient increases 'normally' with T over the range 15° to 35° c. Above $c^{\frac{1}{2}} = 0.15$ the diffusion curves at 15° and 25° are seen to cross. The curves for 15° and 25° are seen to have a large peak at about $c^{\frac{1}{2}} = 0.19$ followed by a drop in D and then an increase. The gradient, $\frac{dD}{dc^{\frac{1}{2}}}$, on the low concentration side of the peak, is seen to be remarkably steep, followed by a less rapid change of D with $c^{\frac{1}{2}}$ on the other side of the peak.

It appears as though some change in the nature of the diffusing particle is occurring. None of the equations described in this section are applicable in this unusual case of tracer diffusion

of a very weak electrolyte. For comparison one may substitute the limiting ionic conductance for Cl^- found in the transference work (part IV) into the Nernst limiting equation (5. 2.4) to obtain

$$10^5 D_{\text{Cl}^-}^{o'} = 3.18, 3.39 \text{ and } 3.51 \text{ cm}^2 \text{ sec}^{-1} \text{ at}$$

15° , 25° and 35° for the free ion. As expected, although the limiting diffusion coefficient appears to increase at higher temperatures (fig. 31), any reasonable extrapolation of the data graphically represented in figure 31 certainly could not produce these values of $D_{\text{Cl}^-}^{o'}$ at infinite dilution. The diffusion coefficient of the undissociated acid at infinite dilution appears to be greater than the limiting diffusion coefficient of the anion. Ion pairing raises the diffusion coefficient compared to the non-paired case, and it seems likely that complexing of the type $(\text{HCl})_x$, which is polymerization of HCl molecules, will also raise D with respect to the monomer. If $x = n$ then there will be less resistance to diffusion of $(\text{HCl})_n$ than to n separate HCl molecules. The peaks at $c^{\frac{1}{2}} = 0.19$ in the figure, for 15° and 25° , could thus be qualitatively explained by assuming existence of HCl polymers. It is very likely that these polymers are in equilibrium with similar polymers of different size, the picture being a statistical one. The stability and hence nature of the polymers seems to vary with concentration, which is not unexpected.

If on the other hand, one assumes existence of $(\text{HCl})_x - (\text{acetone})_y$ complexes, it seems probable that the diffusion coefficient of such a complex will be less than for diffusion of

HCl alone. The shape of the two curves could then be explained by a change in the degree of solvation of hydrogen chloride molecules as the concentration changes from 0.004 to 0.1 molar, the peaks corresponding to a lesser degree of solvation.

Both types of complex were suggested from conductivity results.^{29,16} However, the solvated complexes have only been suggested at temperatures below 0° C and for this work the polymer type complex is the preferred assumption.

The relationship of the curve at 15° to that at 25° is interesting. In general one expects ¹⁴⁵ diffusion to proceed more rapidly at higher temperatures. Figure 31 shows that at lower concentrations (below about $c^{\frac{1}{2}} = 0.15$ M) the diffusion coefficient is indeed greater at the higher temperature. However, as polymerization (assuming this is so) proceeds the polymers appear to be more stable, and therefore the average degree of polymerization is larger, at the lower temperature, which is ¹⁴⁵ eminently reasonable. Any attempt to estimate activation energies from the available data would not be meaningful, as the activation energies of diffusion and complexing are probably comparable and unknown, and the diffusing entities are also unknown.

The above suggestions are, of course, tentative, as were those based on the conductance results and the small, but finite, degree of dissociation which exists must also be considered.

However, the fact that deductions from these two sources of information are qualitatively compatible is, perhaps, encouraging.

It would be instructive to measure diffusion coefficients and conductances of HBr and even HI in acetone. Similar results might be expected. For more precise evaluation of the results, the recent suggestions of Mills and Godbole¹⁴³ could be used, whereby a single capillary is used and the change of activity with time is continuously measured as diffusion progresses. The precision claimed for this method, 0.1%, is a great improvement on anything previously achieved by the capillary method. The above measurements should be coupled with viscosity and activity coefficient determinations, if possible, to assist in interpretation.

The need for further theoretical and experimental work in the field of dilute weak electrolyte diffusion is obvious.

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